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The dielectric behaviour of polycrystalline $Ba_{0.96}Na_{0.04}Ti_{0.96}Nb_{0.04}O_3$ solid solution

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ABSTRACT

Purpose: The purpose of this work was to measure and investigate dielectric properties of new material, polycrystalline solid solution $Ba_{0.96}Na_{0.04}Ti_{0.96}Nb_{0.04}O_3$ (BNTN4) within the temperature range 153 K-473 K.

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

Findings: The dielectric permittivity(ε') dependence on temperature (T) within the range of 473 K-225 K consist of two components: the reversly proportional one and the second one in the form of small local, transient peak at about 400 K. The global maximum is frequency dependent and above ~400 K along the T decrease, the dispersion of ε' is initiated and low frequency dispersion of ε' prevails below 250 K. Energy losses measure (ε"), correlated with ε'(T), is generally shifted towards lower T values. Its frequency dependence undergoes inversion which develops with T decrease and is initiated at about 370 K. The whole temperature induced phase transition turned out to be of relaxor kind and diffused process. The detailed analysis of this transition and its features was performed.

Research limitations/implications: In order to determine the details of polycrystalline structure of BNTN4 new material for modelling of ferroelectric properties the precise X-ray diffraction measurements should be performed as function of T. The nature of ferroelectric - paraelectric (FE - PE) transition diffusive character will be studied by means of dielectric measurements within frequency range 1 MHz-1.8 GHz.

Originality/value: The new kind of ferroelectric solid solution (BNTN4) was synthesized. The specific features of this material at low T range involves among others, the T-dependent dispersion of dielectric properties on low T side of broad ε'(T) peak.

Keywords: Polycrystalline; Phase transitions; Ferroelectrics; Relaxor; Dielectric spectroscopy

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MATERIALS

1. Introduction

The searching of new materials with perovskite structures is inspired among others, also by new technical applications [1]. The investigations of theirs dielectric properties involves mainly phase transitions[2-5], piezoeffect and pyroeffect [6], as well as domain structure [7]. Structural and calorimetric investigations are sources of practically important information [8]. Environment protection also forms a new standards to be meet by new materials [9]. Ferroelectric solid solutions synthesized on the basis of barium titanate (BT) and $NaNbO_3$ (NN) do not contain lead and possess many interesting dielectric properties [10]. In the

literature of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ one can resolve three kinds of ferroelectric behaviour [11, 12]. For composition within the range of $0 \le x \le 0.075$, this materials are mainly of classical ferroelectric character. Within the $0.075 \le x \le 0.55$ range, the solid solutions of relaxor character can be prepared. For higher range of x, materials in which the phase transitions occurs, typical for ferroelectrics and antiferroelectrics. BT as an archetypical ferroelectric with perovskite structure, shows three structural, dielectrically active transitions: at 183 K the transition from rhomboedric structure to orthorhombic one, at 268 K from orthorhombic to tetragonal one and at 393 K from tetragonal to cubic one. This last one have also character of FE - PE transition [13]. The NN also of perovskite structure at room temperature, is antiferroelectric with orthorhombic structure. Phase transition of NN involves two structural transitions: at 400 K to tetragonal phase and at 600 K to cubic one [14]. In this work we aimed at preparing a new polycrystalline, solid solution BNTN4 and to investigate the dielectric properties of this material, especially the FE - PE phase transition.

2. Experimental

The ceramic sample of BNTN4 was prepared by means of calcinations method [2, 4] 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 during 2 h. Next the mixture was dried, pressed and synthesis was thermally initiated. Temperature and time of synthesis duration was 1340 K and 15 h. Than, samples were grained again, pressed and sintered at 1460 K by 2 h. The real density of final ceramic equals 4.62 g/cm^3. Samples in the shape of disc-pellets sized 9.0 mm (diameter) and 1.4 mm (thick) 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 and electric modulus were performed using standard dielectric spectroscopy in the frequency range between 20 Hz and 1 MHz [15, 16]. Amplitude of measuring voltage was 1 V.

3. Results and discussion

Both parts of complex dielectric permittivity of BNTN4 as functions of T for three selected frequencies of measuring electric field are shown in the Fig. 1. The ε'(T) along T decrease is rising up within the range from 473 K to about 225 K, where it achieves maximum with position and value dependent on frequency and temperature. Initially, this grow is almost of linear shape and frequency independent. The dispersion is growing slowly and their full form it achieves after maximum. At ~400 K there is small local nonlinearity of transient nature. It can originate from BT fraction within the sample structure. One can introduce it as an approximation in the form of small Gaussian contribution localized with its maximum at 400 K. The highest values of ε'(T) takes place for the lowest frequency and T values. Generally, there are three stages of polarizability and dielectric energy losses evolution along T decrease. The first one extends within (473 K - ~ 375K), the second up to the 225 K and the last one after ε'(T) maximum. The whole process is identified as FE - PE phase transition of relaxor kind. All stages of ε''(T) within T scale are shifted towards lower temperatures as related to appropriate stages of ε'(T). For 1 MHz this shift amounts about 70 K. It is typical for relaxor behaviour. As a whole, phase transition presented in the Fig. 1 is not typical example of solid solution dielectric behaviour. The further investigation involving X-ray diffraction measurements of physical structure evolution is needed for closer modelling of character of this ferroelectric transition. It is connected with unsolved question of interplay between physical structure activity and dielectric activity only induced thermally and measured in macroscopic scale as dielectric properties evolution.

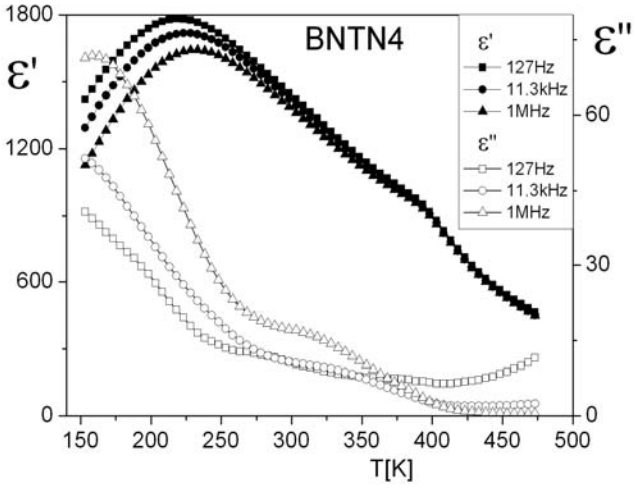

Fig. 1. The dependence of real (ε') and imaginary (ε'') parts of dielectric permittivity on temperature and frequency for BNTN4

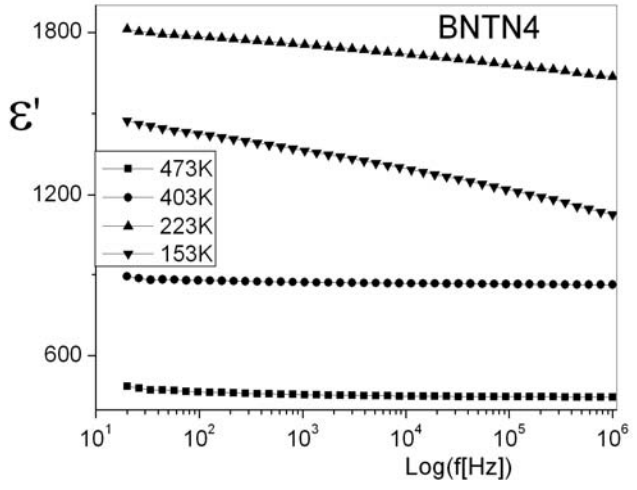

Fig. 2. The dependence of real part of permittivity (ε') on frequency for BNTN4 at selected constant temperatures

In order to illustrate the character of ε'(f) dispersion within the whole frequency range applied in our measurements, the dependence of ε' on frequency for temperatures ranges of ferroelectric and paraelectric phases are shown in the Fig. 2. Below the transition T, the dispersion characteristic for relaxors is seen (153 K and 223 K). Above this temperature, permittivity values are frequency independent. Energy losses in ε"(f) representation and in log–log scales, versus frequency are presented in the Fig. 3 for the same temperatures as in former figure. The phase transition changes the energy losses dispersion slope very slight. For high temperatures losses are week frequency dependent and are higher for higher frequencies and have almost the same slope for both temperatures. After transition, for low T values the share of high frequencies components is substantially reduced.

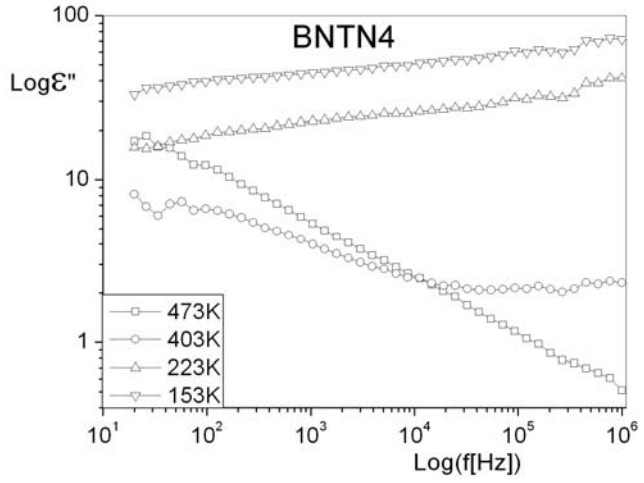

Fig. 3. The dependence of dielectric energy losses on frequency for BNTN4 at selected constant temperatures

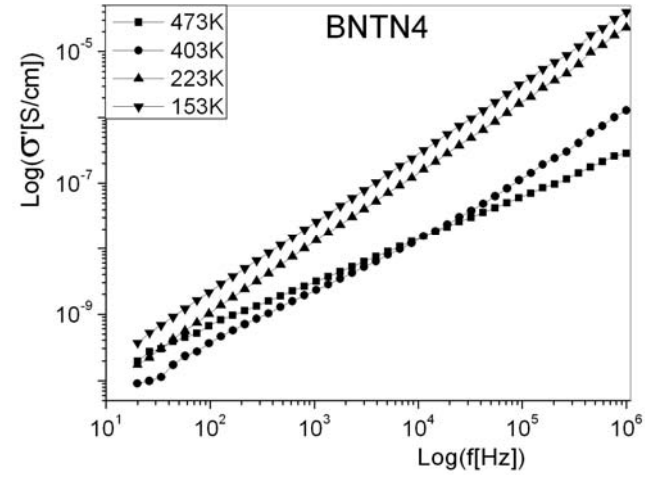

Fig. 4. The dependence of real part of ac conductivity (σ') on frequency for BNTN4 at selected constant temperatures

Another representation of energy losses are presented in the Fig. 4. It is the dependence of ac real part conductivity (σ') on frequency for selected temperatures as before. The comparison of dispersion and absorption (both last figures) points out on dominating of bonded charge in dielectric losses. These are dipoles within polar regions and ferroelectric domains.

It is confirmed by the fact illustrated in the Fig. 5, where functions 1/ε'(T) and real part of electric modulus, M'(T) are identical within the scale of measurement used. It means that ε" values are negligible as compared to ε'. For paraelectric phase, 1/ε'(T) graphs were applied to checking the Curie-Weiss rule. They showed a substantial discrepancy. Within the T range from 218 K to 400 K nonlinearity is observed. Above 400 K, there is linear behaviour but some small differences in slops occurs. Values of C and T_0, constants equals $0.69 \cdot 10^5$ K and 325 K for 127 Hz and $0.64 \cdot 10^5$ K with 330 K at 1 MHz.

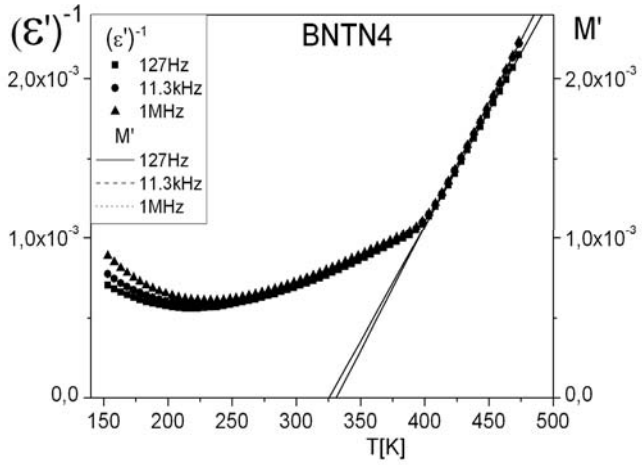

Fig. 5. The inverse of real part of permittivity (1/ε') and real part of electric modulus (M') as a functions of temperature at chosen frequencies for BNTN4 sample

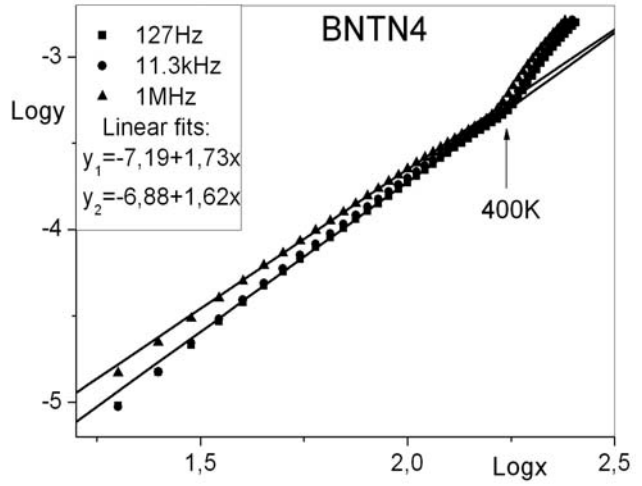

Fig. 6. The dependence of log(y) on log(x) for BNTN4 sample (for abbreviations see text)

Thus simple linear fitting in the form of Curie-Weiss dependence can not be applied and the following relation was

introduced [3] in order to describe dielectric permittivity dependence on temperature:

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

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 $\gamma = 1$ and for diffusive transitions it approaches about 2. It can be seen from Fig. 6, where the (1) dependence was linearized by means of the following abbreviations:

$$y = \varepsilon^{-1} - \varepsilon_m^{-1} \quad (2)$$

$$x = T - T_m \quad (3)$$

The dependence in the Fig. 6 is presented in the form of logy = f(log(x)) for chosen frequencies. The two linear fits as functions of frequency (equation (1)), gave two γ values: for paraelectric phase (up to 400 K) $\gamma_1 = 1.73$ at 127 Hz, and $\gamma_2 = 1.62$ at 1 MHz. Above T = 400 K, which corresponds to phase transition FE - PE in BT and also to structural transition in NN, values of γ get values greater than 2. Such dielectric behavior in case of BNTN4 points out on complex nature of diffusivity of phase transition FE - PE in this new material.

4. Conclusions

The new polycrystalline solid solution material BNTN4 was synthesized by means of classical method. The dielectric characteristic of this material was performed and analysed. Not typical dielectric behavior was observed. The phase transition of FE - PE kind turned out to be of diffusive character. The specific features of this transitions were described on both sides of this transition. The features of dispersion nucleation and thermally induced development as well as reversed frequency dependence of energy losses were described.

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