Archives of Materials Science and Engineering

Volume 39
Issue 2
October 2009
Pages 107-110

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Dielectric spectroscopy study of $Ba_{0.98}Na_{0.02}Ti_{0.98}Nb_{0.02}O_3$ ceramic

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Received 21.07.2009; published in revised form 01.10.2009

ABSTRACT

Purpose: The purpose of this work was to investigate dielectric properties of new ceramic solid solution $Ba_{0.98}Na_{0.02}Ti_{0.98}Nb_{0.02}O_3$ (BNTN2) within the temperature range 153 K - 473 K.

Design/methodology/approach: The dielectric spectroscopy method was applied to measure frequency and temperature dependence of complex dielectric permittivity, complex admittance, phase angle. The frequency dependence of ac conductivity at constant temperature was analysed as well as reciprocal permittivity and dielectric modulus as functions of temperature and frequency were compared. The Curie-Weiss rule and its generalized formula were applied in outcomes analysis.

Findings: The ferroelectric - paraelectric (FE - PE) phase transition occurring in BNTN2 was found as having diffusive nature. In the paraelectric phase at about 400 K the diffusivity of transition step is correlated with the same kind of transition in $BaTiO_3$ (BT) (transition of FE - PE type) and with structural transition occurring in $NaNbO_3$ (NN). Within the temperature range below T_m = 308 K, dependences of dielectric properties of BNTN2 ceramic on temperature and frequency was found as having relaxor type of behaviour.

Research limitations/implications: The confirmations of achieved findings will be possible by more precise BNTN2 structure determination by means X-ray diffraction. Also closer explanation of FE - PE phase transition can be performed by dielectric measurements within broader frequency range up to 1.8 GHz (diffusive versus relaxor character of transition).

Originality/value: The new solid solution of BNTN2 was prepared. The structure of this material was characterized as dielectrically active and having FE - PE phase transition which was described.

Keywords: Ceramics; Phase transitions; Ferroelectrics; Dielectric spectroscopy

Reference to this paper should be given in the following way:

W. Bąk, M. Gabryś, C. Kajtoch, K. Stanuch, F. Starzyk, Dielectric spectroscopy study of $Ba_{0.98}Na_{0.02}Ti_{0.98}Nb_{0.02}O_3$ ceramic, Archives of Materials Science and Engineering 39/2 (2009) 107-110.

PROPERTIES

1. Introduction

Ferroelectric oxides with perovskite structures are subject of many investigations. It is motivated by their practical applications. They involve mainly piezoelectric and pyroelectric effects [1], domain structure [2] and phase transitions [3-6]. These properties are practically applied in many branches of technique [7]. Recently, the ferroelectrics, environment friendly, without lead components, are also investigated [8]. The ferroelectric solid solutions synthesised on the basis of BT - NN compounds seemed to possess many interesting dielectric properties [9]. In the case of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ one can specify three types of ferroelectric behaviour dependently on its composition [10, 11]. Within the range $0 \leq x \leq 0.075$ samples of this material behaves like classical

ferroelectric with sharp phase transitions. For $0.075 \le x \le 0.55$ this material is described as relaxor type ferroelectric. Within the range of $0.55 \le x \le 1$, one can found these structures being classified as classical ferroelectric or antiferroelectric. BT with perovskite structure undergoes 3 structurally active phase transitions: at the temperature 183 K (from rhomboedric to orthorhombic ones), at 268 K (from orthorhombic to tetragonal) and at 393 K, the tetragonal to cubic one which is also of FE - PE type [12]. NN with perovskite structure has antiferroelectric properties and is orthorhombic at room temperature. It gets two structurally active phase transitions, at 400 K to tetragonal structure and at 600 K to cubic one [13]. In this work we aimed at phase transition of FE - PE type investigation in BNTN2 ceramic solid solution.

2. Experimental

The ceramic sample of BNTN2 was 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 during 2 h. Next the mixture was 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 at 1420 K by 2 h. The real density of final ceramic equals 5.37 g/cm^3. Samples in the shape of disc-pellets sized 9.70 mm (diameter) and 1.77 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 used heating and cooling agent 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 between 20 Hz and 1 MHz [14, 15]. Amplitude of measuring voltage was 1V.

3. Results and discussion

Measurements outcomes were collected and expressed in the form of complex dielectric permittivity, electric modulus and admittance as functions of temperature and frequency. Additionally, the phase angle (Φ) and ac conductivity (σ) were measured and analysed. The dependence of real (ε') and imaginary (ε") parts of dielectric permittivity on temperature and selected frequency values for BNTN2 are shown in the Fig.1. These dependencies point out on diffused character of investigated phase transition: FE - PE one. Temperatures at maximums of ε' (Fig.1) for all frequencies used are of the same value and equals 308 K. In the case of BNTN2 structure, there are no characteristic three maximums occurring in the case of BT where classic phase transitions of I or II kind takes place. Noticeable but very small change of exponential character of ε'(T) function takes place at about 400 K. One should keep in mind that at this temperature in the BT and NN cases structural transitions occur (tetragonal to cubic and from orthorhombic to tetragonal). Additionally in BT sharp FE - PE phase transition takes place. The BNTN2 material was prepared on the barium titanate with only 2 % NN admixture. It turned out that such small NN admixture amount makes very drastic change of these new material ferroelectric properties. Despite the fact that for all frequencies used (Fig. 1) maximum of ε'(T) function occurs for the same temperature (308 K). The BNTN2 have also features characteristic for relaxors. For temperatures below phase transition, differences of ε' for different frequencies are also visible. For lower frequencies permittivity values are higher (127Hz). Also the ε"(T) values and shape are typical for relaxor behaviour. Dielectric losses are higher for higher frequencies (1 MHz). The temperature of ε"(T) maximums is shifted down from 233 K (at 1 MHz) to 203 K (at 127 Hz). The most important feature of BNTN2 new material is that below the phase transition temperature (308 K), it demonstrates all characteristic relaxor features. Above this temperature, ε'(T) function is typical for diffused phase transitions.

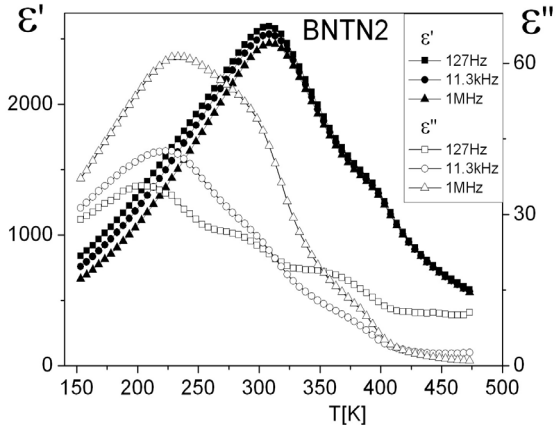

Fig. 1. The dependence of real (ε') and imaginary (ε") parts of dielectric permittivity on temperature and frequency for BNTN2

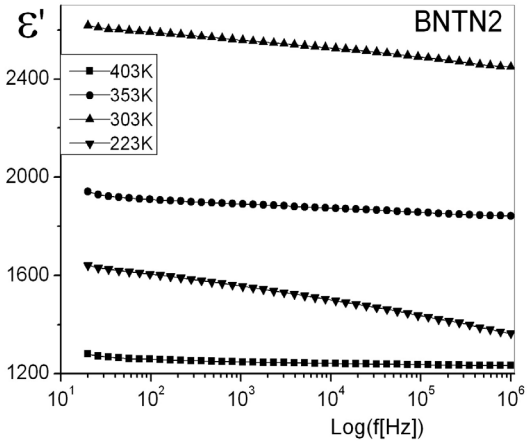

Fig. 2. The dependence of real part of permittivity (ε') on frequency for BNTN2 at selected constant temperatures

The dispersion character of ε'(f) function for selected temperatures below and above T = 308 K is presented in the Fig. 2. Below this temperature value the very weak dependence on frequency is visible and this is typical for relaxors. Above in turn, for higher frequencies dispersion effectively disappears.

Dielectric losses of energy expressed by real part of ac conductivity are illustrated in the Fig. 3. In order to compare dielectric dispersion and absorption in both (Fig. 2 and Fig. 3), permittivity dependence of frequency (ε'(f)) and real conductivity dependence on frequency (σ'(f)) are presented for the same selected temperature values. The fit of σ'(f) in log-log scale for temperatures below 308 K gave the slop value close to 1. Thus, if points up on the share of bonded charges in dielectric losses. Above this temperature the σ'(f) function character implies, especially for low frequencies, elevated share of free charges in losses.

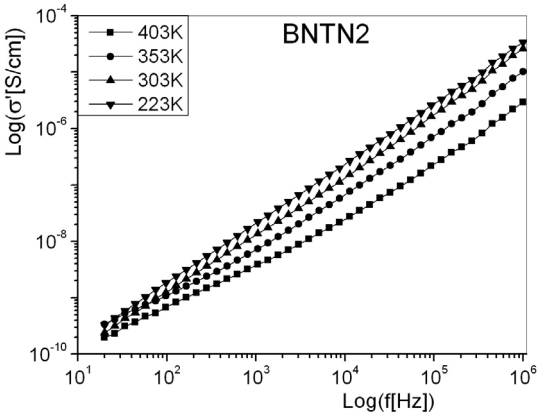

Fig. 3. The dependence of the ac conductivity real part (σ') on frequency for BNTN2 at selected constant temperatures

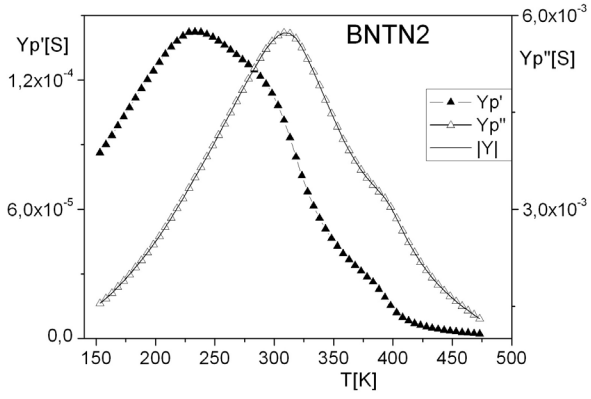

Fig. 4. The dependence of real (Yp') and imaginary (Yp") parts of admittance on temperature at 1 MHz for BNTN2. Additionally, the admittance modulus versus temperature is shown for the same frequency

The dependence of real Yp'(T) and imaginary Yp"(T) parts of electric admittance as well as of its modulus |Y| on temperature for 1MHz is demonstrated in the Fig. 4. Values of Yp"(T) function and |Y|(T) are identical within the scale of observation. It means that Yp"(T) values dominates. They are connected with the sample capacity (and energy losses) and with ε'(T) function. The Yp'(T) in turn corresponds to ε"(T) function. The temperature change induced evolution of dielectric losses expressed by Yp'(T) and by phase angle Φ(T) evolution is presented in the Fig. 5. The maximum of Yp'(T) at 203 K corresponds to ε"(T) maximum at the same temperature value (Fig. 1).

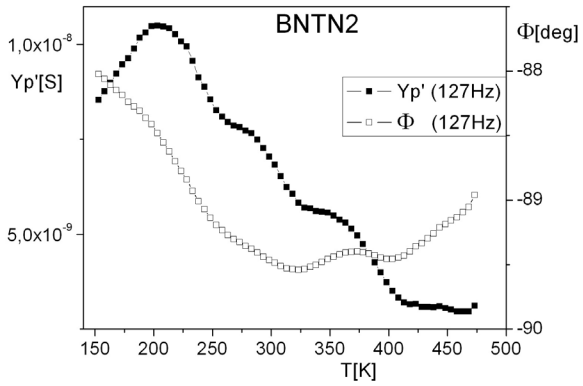

Fig. 5. The dependence of real part of admittance (Yp') on temperature together with phase angle (Φ), both for BNTN2 and low frequency (127 Hz)

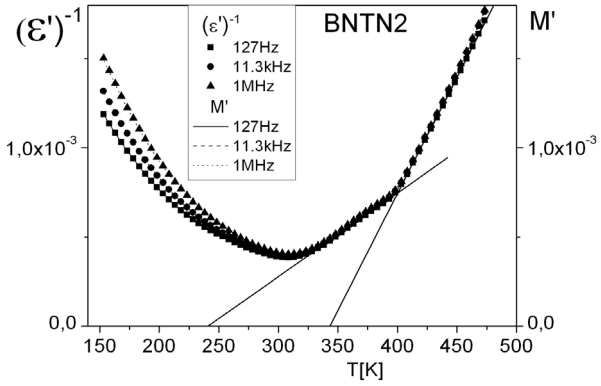

Fig. 6. The inverse of real part of complex dielectric permittivity (1/ε') and real part of electric modulus (M') as a function of temperature at chosen frequencies for BNTN2 sample

The dependence of 1/ε'(T) and electric modulus M'(T) on temperature at selected frequencies for BNTN2 sample is presented in the Fig. 6. Within the whole used temperature and frequency ranges both functions have identical values in the used observation scale. It implies that BNTN2 new material is low loss dielectric. But another advantage of the way of data presentation and analysis we applied (Fig. 6) is the possibility of resolving three ranges of temperature and to prescribe them well separated features as follows: down from about 330 K one can see thermally induced dispersion of dielectric polarizability of new presented material BNTN2; for temperatures higher than about 330 K the well established lack of dielectric dispersion is visible.

The characteristic braking point at about 400 K separates the range of high temperatures into two linear well established ranges with two slopes of values enabling closer interpretation of dielectric activity of structural transition taking place in this temperature range. The next important feature separation implying from the way of data presentation (Fig. 6), is the value of about 330 K, the temperature at which the dispersion initiation begins together with temperature decrease. The interpretation of

this temperature physical meaning will be a subject of further detailed investigation, experimental and of model kind. For paraelectric phase range, above T > 308 K, 1/ε'(T) function obeys the rule of Curie-Weiss. Values of constants C and T_0 determined by means of linear regression for BNTN2 in temperature range 308 K - 400 K equals: $C = 2.10 \cdot 10^5$ K and $T_0 = 240$ K. Within the temperature range 400 K - 473 K those constants got values: $C = 0.76 \cdot 10^5$ K and $T_0 = 343$ K.

The geometric interpretation of Curie-Weiss rule 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:

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

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

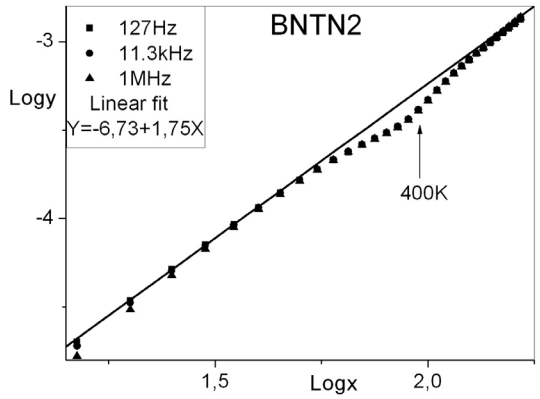

Fig. 7. The dependence of log(y) on log(x) for BNTN2 sample (for abbreviations see text)

In the case of classical phase transitions γ = 1 and for diffusive transitions it approaches about 2. It can be seen from Fig. 7, 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. 7 is presented in the form of logy = f(log(x)) for chosen frequencies. For the BNTN2 (Fig. 7) there are also two linear ranges visible. In this representation, the general trend is represented as a linear fit demonstrated in the figure. The slop of the linear fit gives a value of γ = 1.75 which indicates a transition with diffused character. The temperature ~400 K visible in the Fig.6, is visible in the representation used in the Fig. 7 as local declination from linear trend. Because this temperature value coincides with those of FE - PE phase transition in BT and also with structural transition in case of NN, one can stated that for BNTN2 new material the ~400 K points on the temperature scale represents local BT-type behaviour memory.

4. Conclusions

The new solid solution BNTN2, was prepared by means of calcinations method. The dielectric properties described in this work are the first ones published. The temperature sensitive mixed nature of FE - PE phase transition in this material was investigated within the temperature range from 473 K to 153 K and frequency range from 20 Hz to 1 MHz. It was established that phase transition of FE - PE nature is of diffused type and that at ~400 K, specific for BT, can be treated as thermally induced local BT property of structural memory character. Additionally below the 330 K, with temperature lowering, a process of permittivity dispersion increase is initiated. It is probably the origin of relaxor type of behaviour on this side of temperature range. On the basis of generalized Currie-Weiss rule, above 308 K the character of this transition diffusivity was demonstrated. This new material will be a subject of further detail investigations and modelling.

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