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Relaxor properties of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ at low temperatures

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ABSTRACT

Purpose: The purpose of this paper is to investigate ferroelectric relaxor behavior of polycrystalline solid solutions of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ (for x = 0.3 and x = 0.4) at low temperatures (113 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: Temperature dependences of real (ε') and imaginary (ε") parts of dielectric permittivity confirm relaxor type of polarization behavior for both investigated materials. Experimental findings are in good agreement with data published in literature. Diffused phase transition of relaxor character is analysed in the terms of departure from Curie-Weiss rule. A dependence of the temperature related to the maximum of dielectric permittivity on the frequency has activated character. Different thermal activation energies found for the investigated materials may be related to their different microstructures.

Research limitations/implications: Further investigations should be carried on in a broaden frequency range (up to 1.8 GHz) in order to establish an influence of network dynamics on ferroelectric-paraelectric phase transition.

Originality/value: Relaxor behaviour in polycrystalline solid solution of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ (for x = 0.3 and x = 0.4) is described.

Keywords: Ceramics; Relaxor; Electrical properties; Dielectric relaxation spectroscopy

PROPERTIES

1. Introduction

Relaxor ferroelectric oxides with perovskite structure are subject of many investigations because of both theoretical and practical reasons. In case of ferroelectric relaxors, spontaneous polarization occurs well above the phase transition temperature [1]. Additionally, relaxors exhibit strong dielectric dispersion. The dielectric permittivity dependences on temperature and frequency are used to describe phase transitions of sharp character (first and second order type) as well as diffuse or relaxor ones [2, 3].

Relaxor type behavior was established mainly in the materials containing lead, like $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [4]. Recently, lead – free materials are looked for because of their environment friendly character. These materials possess high piezoelectric constants and are widely applied in technics [5, 6]. Two classical nonrelaxors with perovskite structure were selected for investigation: $BaTiO_3$ [7] and $NaNbO_3$ [8]. The solid solution of these materials ($BaTiO_3$ - $NaNbO_3$) creates the structure with relaxor polarization behavior [9]. According to [10], $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$, may exhibit different ferroelectric behavior. For $0 \le x \le 0.075$, the classic typical ferroelectric materials are formed. When x is contained between 0.075 and 0.55 the solid solution is classified as relaxor type. Finally, within the range of $0.55 \le x \le 1$, ferroelectric or antiferroelectric behavior is observed. The dielectric properties of ferroelectrics, in general, and perovskites, in particular, can be modified by a substitution of ions with different valence [11] into cationic subnets: both A, B or A and B type. The dielectric absorption and dispersion can be also modified by a substitution of nonferroactive ions, like Sn [12], into B subnet.

The purpose of this work is to investigate a dependence of dielectric properties of polycrystalline samples of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ solid solution (for x = 0.3 and x = 0.4) on the temperature and frequency.

2. Experimental

Two ceramic samples were obtained: $Ba_{0.7}Na_{0.3}Ti_{0.7}Nb_{0.3}O_3$, (BNTN03) and $Ba_{0.6}Na_{0.4}Ti_{0.6}Nb_{0.4}O_3$, (BNTN04). The samples of 7 mm diameter and 1 mm thickness were prepared by means of conventional method using $BaTiO_3$ and $NaNbO_3$ [13]. The real ceramic density in the case of the sample sintered at 1573 K equals 3440 kg/m^3. Electric contacts were prepared by means silver conducting paint. All measurements were performed with application of QUATRO KRIO 4.0 temperature system together with precise LCR Agilent 4284A meter, BDS 1100 cryostat and WINData 5.62 software Novocontrol. The data were taken at stabilized temperature points within the range from 473 K to 113 K with 5 K step. Measurements of dielectric permittivity and dielectric loss coefficient were performed using standard dielectric spectroscopy in the frequency domain between 20 Hz and 1 MHz. Amplitude of measuring voltage was 1 V. Complex permittivity, impedance, admittance, and electric modulus were measured [14, 15].

3. Results and discussion

Temperature dependence of real (ε') and imaginary (ε'') parts of dielectric permittivity of BNTN03 and BNTN04 are shown in Fig. 1 and Fig. 2. The curves have been drawn for 5 selected frequency values differing by about one – order of the magnitude. The character of ε'(T) shape confirms phase transition between ferroelectric and paraelectric phases. Additionally, the ε''(T) functions for both investigated materials exhibit relaxor character. It is in agreement with literature reports [1, 9]. Maximum value of ε'(T) shifts down with an increase of x ($NaNbO_3$). Above this maximum, a strong dielectric dispersion is visible as the temperature increases. The frequency increase lowers the maximum of ε'(T) and shifts it towards higher temperatures. Such behavior is specific for relaxor type of ferroelectricity. It can be connected with a distribution of the substituted ions in cationic subnets. For ferroelectrics with diffused phase transition, the temperature lowering from the temperature above paraelectric – ferroelectric phase transition is followed by nucleation of the dipoles and next by formation of the polar regions. At the temperatures close to the phase transition a coexistence of the ferroelectric domains with the small polar regions occurs. Thus, external electric field induces dielectric response originating from these two types of polar species. The strong dielectric losses are manifested by the character of ε''(T) function, typical which is for relaxor behavior. With the frequency increase, the ε''(T) maximum rises and shifts towards higher T.

The dependence of 1/ε'(T) versus temperature, obtained for BNTN03, is shown in Fig. 3. Because dielectric responses of both samples are similar, Curie – Weiss dependence has been demonstrated only for BNTN03 sample. The linear fit has been made for the frequency equal to 1 MHz (Fig. 3). It points out two characteristic temperatures: T_o – related to Curie – Weiss temperature and T_{dev}, at which ε'(T) declines from the Curie – Weiss run. Additionally, the T_m temperature has been assigned. It is the temperature of ε'(T) maximum.

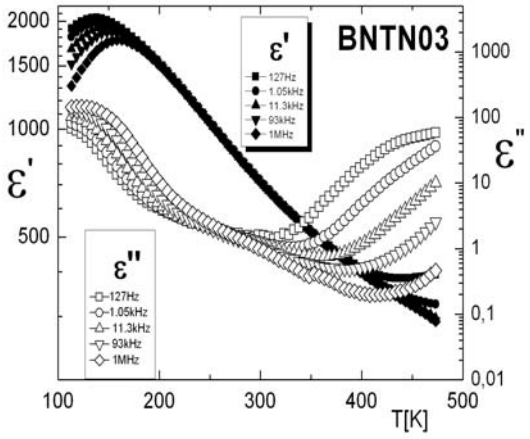

Fig. 1. Temperature dependence of real (ε') and imaginary part of permittivity (ε'') for BNTN03

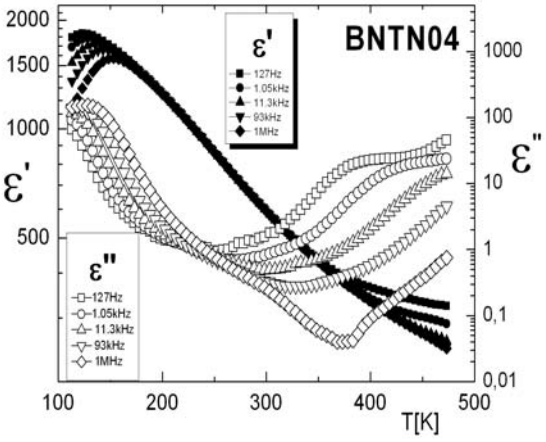

Fig. 2. Temperature dependence of real (ε') and imaginary part of permittivity (ε'') for BNTN04

A correlation of the maximum values of ε'(T_m) with the frequency is shown in Fig. 4. The character of the obtained dependences gives an additional confirmation of the relaxor properties of the investigated materials. The same dependences are presented in Fig. 5 but for T_o and T_{dev} temperatures. The difference between these temperatures equals about 100 K and can be treated as a measure of a declination from classical ferroelectric behavior. The dependence of the frequency against reciprocal of T_m is demonstrated in Fig. 6. The linear fits are well correlated for both

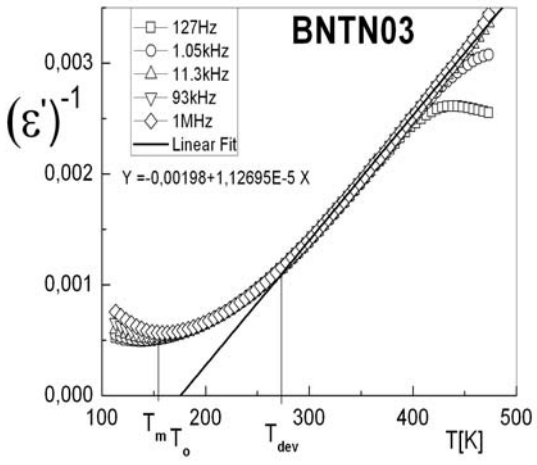

Fig. 3. Inverse of real permittivity (1/ε') as a function of temperature at chosen frequencies for BNTN03

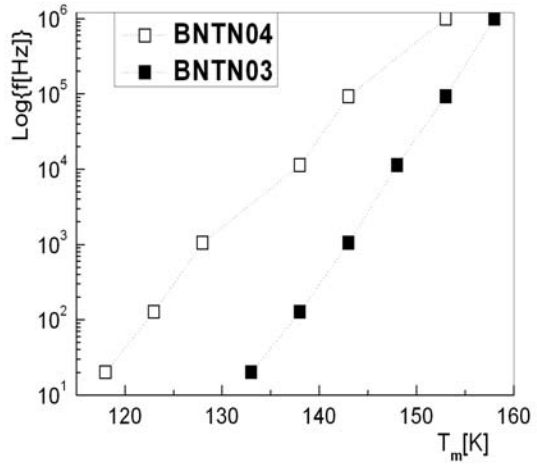

Fig. 4. Frequency versus of T_m for BNTN03 and BNTN04

samples. This supports a relaxational mechanism of dielectric losses and may be well described as Arrhenius formula [9].

The thermal activation energies (for flipping) equal appropriately: (0.79 ± 0.03) eV for BNTN03 and (0.48 ± 0.02) eV for BNTN04. Such values are typical for semiconductors and can be related to the dynamics of polarization changes as well as to dielectric losses at the phase transition of relaxor type.

4. Conclusions

The polycrystalline samples of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ (for x = 0.3 and x = 0.4) were investigated by means of dielectric spectroscopy within the frequencies 20 Hz - 1 MHz and the temperatures from 473 K to 113 K. The results confirmed the relaxor behavior of the polarization for the investigated materials. They are in agreement with those published in the literature. The results indicate the diffused character of the phase transition within the low temperature region. The magnitude and character of declination from the Curie – Weiss law described by the frequency dependence, also confirm the relaxor behavior.

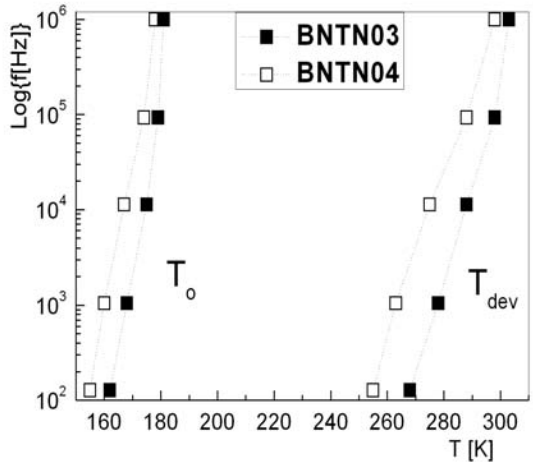

Fig. 5. Frequency versus T_0 and T_{dev} for BNTN03 and BNTN04

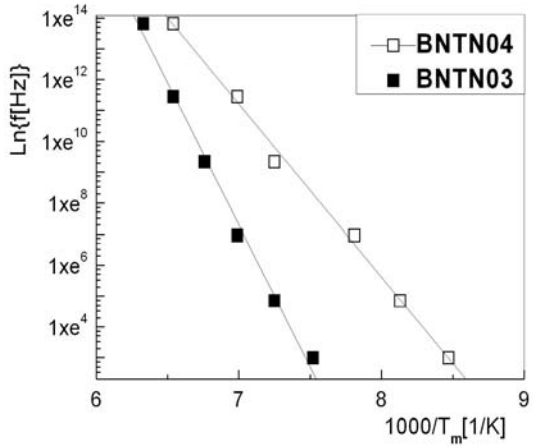

Fig. 6. Frequency versus reciprocal temperature for BNTN03 and BNTN04

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