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Author: W. Bąk, F. Starzyk, C. Kajtoch, Ewa Nogas-Ćwikiel

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Elevated temperature induced dispersion phenomena in Ba$_{1-x}$Na$_x$Ti$_{1-x}$Nb$_x$O$_3$

W. Bąk [a,*], F. Starzyk [b], C. Kajtoch [a], E. Nogas-Ćwikiel [c]

[a] Institute of Physics, Pedagogical University, ul. Podchorążych 2, 30-084 Kraków, Poland
[b] Institute of Physics, Technical University, ul. Podchorążych 1, 30-084 Kraków, Poland
[c] Faculty of Computer Science and Materials Science, University of Silesia,
ul. Śnieżna 2, 41-200 Sosnowiec, Poland
* Corresponding author: E-mail address: wbak@ap.krakow.pl

ABSTRACT

Purpose: of this paper was to investigate features of the dispersion of dielectric permittivity induced by elevated temperature (473K-723K) in polycrystalline solid solution of Ba$_{1-x}$Na$_x$Ti$_{1-x}$Nb$_x$O$_3$ (for x=0.3 and x=0.4).

Design/methodology/approach: used to perform this purpose was dielectric spectroscopy application to measure dielectric and electric parameters within the frequency range (20Hz-1MHz).

Findings: Analysis of temperature and frequency dependences of real (ε') and imaginary (ε") parts of dielectric permittivity had pointed out on relaxor type of dielectric behaviour for both investigated samples in paraelectric phase. The thermal activation energy values of ac conductivity (for 100Hz) are similar to those of semiconductors. Values of ε' for both materials (x=0.3, x=0.4) are consistent with literature quotations. Thus the polarisation behaviour of our materials seems to be similar to those described in the literature. Different behaviour of dielectric energy losses is postulated as originating from differences of samples microstructure.

Research limitations/implications: Further investigations should be carried out in the range of low temperatures (down to 100K) and within a broaden frequency range (up to 1.8GHz) in order to establish the influence of chemical structure on ferroelectric-paraelectric phase transition.

Originality/value: Dielectric properties for two new material prepared from nanopowders of BaTiO$_3$ and NaNbO$_3$ were described.

Keywords: Ceramics; Relaxor; Electrical properties; Dielectric Relaxation Spectroscopy

MATERIALS

1. Introduction

Investigations of basic physical properties of polycrystalic materials are stimulating a knowledge development about new materials structures. They enables designing of new practical applications of these materials [1-3].

Investigation of dielectric permittivity dispersion in ferroelectrics is important because of theoretical and practical reasons. The dispersion is used to classify these materials according to phase transition character e.g. sharp transition of the first and second order as well as diffused transitions or glassy and relaxor type ones [4, 5]. From the practical point of view especially interesting seems to be materials presenting relaxor behaviour. It take place mainly in the case of materials involving lead as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) [6]. But environment friendly materials should not contain lead. These materials can be applied as capacitors and actuators [7, 8]. The dispersion and dielectric absorption character determines functional properties of these ferroelectrics. New materials design relays on the operation of substitution of ions with different valency into cationic sub-lattices A or B / A and B [9, 10]. The dielectric properties of ferroelectrics can be also modified by introducing into sub-lattices nonferroactive ions as Sn [11]. We have focused our

investigations on two classic non-relaxors with perovskite structure, namely $BaTiO_3$ [12] and $NaNbO_3$ [13]. At the room temperature the first one is ferroelectric but the second one is antiferroelectric. The solid solutions based on these two materials with cationic substitutions in both sub-lattices, have got many interesting physical properties of non well understood properties. The aim of this work was to obtain polycrystalline solid solutions $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ having typical relaxors properties as well as investigation of their frequency and temperature dependences of selected physical properties.

2. Description of the materials for research and experiments

The two ceramic pellets were prepared: solid solution of $Ba_{0.7}Na_{0.3}Ti_{0.7}Nb_{0.3}O_3$ (BNTN03) and $Ba_{0.6}Na_{0.4}Ti_{0.6}Nb_{0.4}O_3$ (BNTN04). Pellets were 1mm thick and 7mm diameter. Both samples were prepared by means of conventional method involving $BaTiO_3$ and $NaNbO_3$ nanopowders [14, 15]. Next, dielectric properties were measured by means of ac-technique.

2.1. Preparation

In order to prepare $BaTiO_3$ nanopowder, two precursors were used: barium acetate $Ba(CH_3COOH)_2$ and $Ti(CH_3CH_2CH_2O)_4$. First barium acetate was weighted in the form of white powder. Next it was placed in a flask and acetic acid was added as a solvent. The following step was heating flask content in order to barium acetate dissolution. Than the $Ti(CH_3CH_2CH_2O)_4$ was weight and dissolved in propanol $CH_3CH_2CH_2OH$ during 15 minutes. Both solutions (barium acetate and $Ti(CH_3CH_2CH_2O)_4$) was mixed together in the flask. Achieved mixture was heated during 15 minutes. Further step was mixing of barium acetate solution and $Ti(CH_3CH_2CH_2O)_4$ solution in reflux condenser. Mixture was heated for 15 minutes and it was mixed without heating. As on outcome of chemical reaction running in the flask, after 1h of mixing, the slow gelations of $BaTiO_3$ had initiated. Zol as a hydrolysis results had changed into gel. The gelation of barium titanate was running about 20 minutes. After this time, when gelation had terminated the resulting gel was placed in evaporator. Drying of $BaTiO_3$ gel was carried out during 7 weeks. Gel was transformed into powder. Organic parts of this powders were burned out. The burning process was performed with following conditions: maintaining of maximum temperature – 6h; burning temperature – 1073K; heating speed – 150K/h; cooling – according own cooling. Than nanopowder of barium titanate was grind manually for 2h.

In order to achieve $NaNbO_3$ nanopowder two precursors were used: $NaCH_3CH_2O$ and $Nb(OCH_2CH_3)_5$. The weighted formerly $Nb(OCH_2CH_3)_5$ in yellow powder form was placed in flask. This powder evaporates very fast during weighting. That why in order to avoid weighting errors, the whole contents of $Nb(OCH_2CH_3)_5$ container was poured into flask. Next the sodium ethylate was added. Both reagents were mixed without heating. The rapid egzothermal reaction took place. Resulting solution was of tee-extract-colour and was dense it's temperature equals 353K. The

following step was pouring the vessel contents into evaporator. The liquid density was higher than those of water. Because the achieved solution was not stable, acetyloacetone $(C_5H_8O_2)$ was added as stabilizer. Additionally, 25ml of distilled water was added to initiate hydrolysis of sol and it's transformation into gel. Gelation of sodium niobate nanopowders occurred very fast. After 5 minutes first gel granules were noticed. After about 40 minutes sol had transformed entirely into gel, which was left to dry. Drying was completed after 4 weeks. Again, dry gel of sodium niobate was burned for organic parts removing. The burning conditions was similar as formerly described. The nanopowder was grind manually for 2h.

The weighted portions of $BaTiO_3$ and $NaNbO_3$ powders were grind (for 2h) and mixed together. The next stage was ceramic pressing by means of hydraulic press. The matrix of 8 mm diameter was used. Pressure applied equals 1.6Mpa. The pellets formed were polished and silver paint electrodes were placed on them. Before electrodes painting the real density was determined. It was of the highest value 3440kg/m³ for sintering temperature 1573K.

2.2. Experiments

Before the measurement, each sample was heated for 2h within measuring cell at 723K in order of electric refreshment. All measurements were carried out in air under the normal pressure. Electric measurements were taken under cooling from 723K to 323K with 2K/min speed. Measurements of dielectric permittivity and dielectric loss coefficient were performed using standard dielectric spectroscopy in frequency domain range (20Hz÷1MHz) The current was measured and recorded as response on small sinusoidal voltage excitation [16, 17]. Thus each measurement outcome includes the current amplitude value and phase between this current and voltage applied to a sample. On the basis of the set of these directly measured quantities we obtained the complex impedance, admittance, permittivity and electric modulus values. Real and imaginary parts and also their absolute values of these complex quantities enables to analyse electric properties of samples in the frequency domain. The measurement of chosen complex quantities were carried out by means precise LCR Agilent 4284A meter for five following frequencies: 10^2Hz, 10^3Hz, 10^4Hz, 10^5Hz and 10^6Hz. Amplitudes of measuring voltage were established as 1V and 10V.

3. Results and discussion

3.1. Dielectric properties

The dielectric permittivity (real (ε') and imaginary (ε'') parts) dependence on temperature for BNTN03 sample is presented in the Fig.1 and for BNTN04 in the Fig.2. It is known from literature [7] that phase transition paraelectric-ferroelectric for relaxors with x=(0.075÷0.55) is taking place below 200K. Thus all measurements outcomes presented here are connected with dielectric properties of paraelectric phase. For easy comparing of $\varepsilon'(T)$ and $\varepsilon''(T)$ values of both samples the same temperature scale was used in the figures. The $\varepsilon'(T)$ dependences indicates a typical for paraelectric phase increase with temperature lowering. Some

small declinations of ε'(T) shapes for selected constant frequencies of measuring electric field occurring for both samples above 450K. These changes have probably their origin in complex structure of investigated solid solutions. It can be connected with substitutions of ions in both cationic sub-lattices. One should be keep in mind that along sample temperature decrease (in paraelectric phase) for materials with diffused phase transitions, initially nucleation of dipoles is taking place and further, polar regions as well as ferroelectric domains at paraelectric-ferroelectric phase transition are created. Thus, non-polar paraelectric phase involves "polar" species which interact with external electric field. Consequences of this interaction are manifested itself even more in the case of ε"(T) than for ε'(T). The function ε"(T) strongly depends on frequency. With temperature falling down the ε" values decreases to minimum (for a given frequency) and next they increases back. Positions of these

minimums, starting from T≈600K (10^{6}Hz) and for a given lowering frequency values shifts towards lower temperatures. In the case of BNTN04 sample, below the T≈600K an additional local maximum are observed for 10^{2}Hz, 10^{3}Hz and 10^{4}Hz. They are correlated probably with the structure and relaxation processes and this should be a matter of further investigation. Generally one can notice, according with relaxation phenomena theory, for both samples too, that minimum of dielectric losses (ε") for given frequencies occurs simultaneously with ε' dispersion decay. The dispersion of ε' and associated with it energy loss ε" in the range of elevated temperatures (683K and 723K) for BNTN03 are presented in the Fig.3. The same quantities but for low temperatures (323K and 363K) are collected in the Fig.4. The energy losses (ε") accompanying the strong dispersion of ε', at elevated temperatures have got a visible maximum (Fig.3).
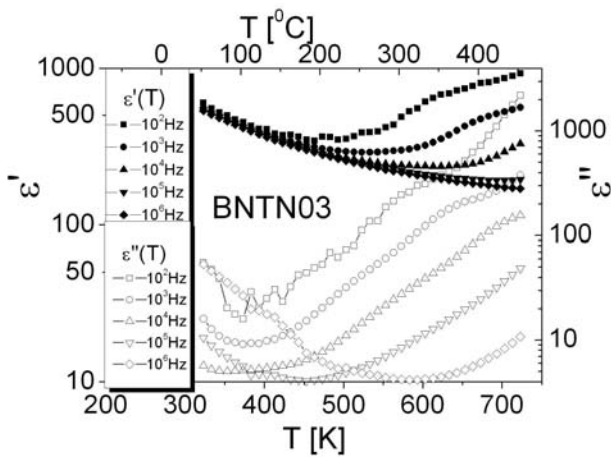

Fig. 1. The dependence of energy storage coefficient (ε') and energy loss coefficient (ε") for BNTN03 sample on temperature. Measurement was taken on cooling
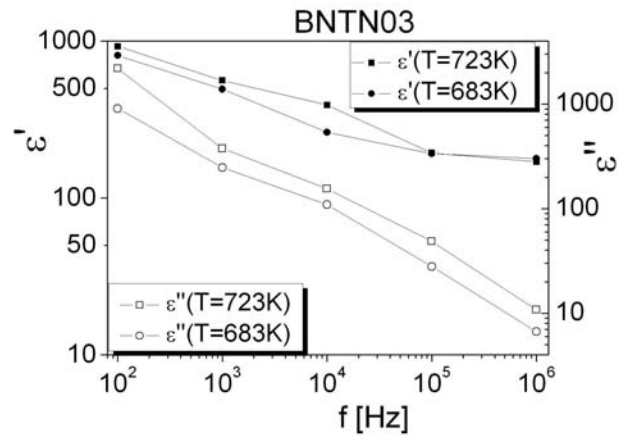

Fig. 3. The dependence of energy storage coefficient (ε') and energy loss coefficient (ε") on frequency at selected, elevated temperatures for BNTN03 sample
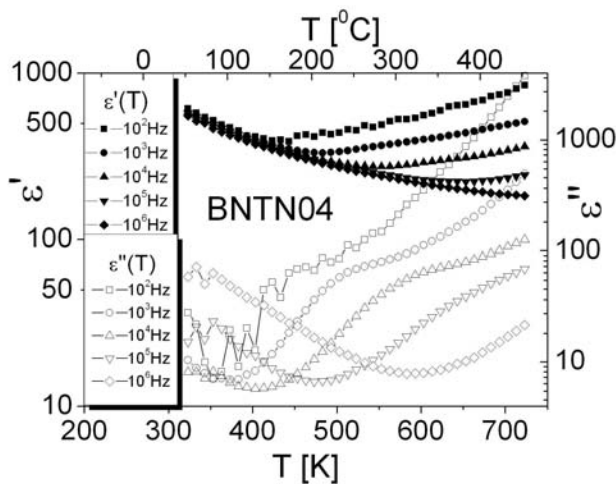

Fig. 2. The dependence of energy storage coefficient (ε') and energy loss coefficient (ε") for BNTN04 sample on temperature. Measurement was taken on cooling
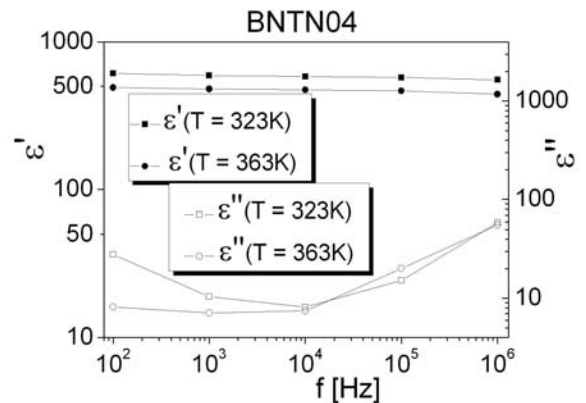

Fig. 4. The dependence of energy storage coefficient (ε') and energy loss coefficient (ε") on frequency at selected temperatures from low temperature region, for BNTN04 sample

The ε" dependence can be treated as typical for materials with dc conductivity is dominating over relaxation processes. It is direct consequence of free charges presence in the sample. In this

work, dielectric loss process is also discussed in the part where ac-conductivity is described. Within low temperatures range (Fig.4), for both samples the dispersion of ε' get 10 times lower values as compared to these for elevated temperatures. Simultaneously, the dielectric losses (ε") for 10^4Hz frequency achieves minimum. That is pointing out on occurring within this temperature range of two different relaxation processes.

3.2. Design of drop forging formed on TSFP

In the temperature range applied in this work, the ac-conductivity can be treated as main dielectric loss component [18]. The ac-conductivity dependence on reciprocal temperature for both samples is presented in the Fig. 5.
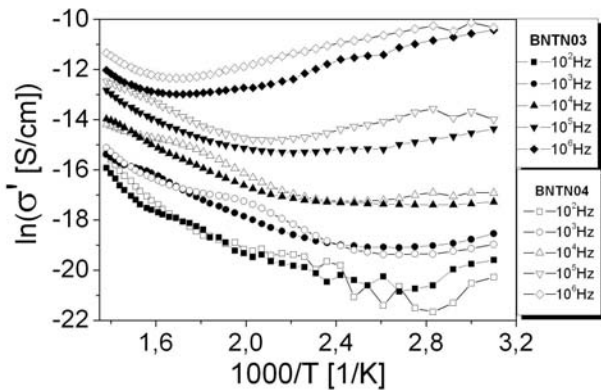
Fig. 5. The ac-conductivity dependence on reciprocal temperature, taken under cooling for BNTN03 and BNTN04 samples
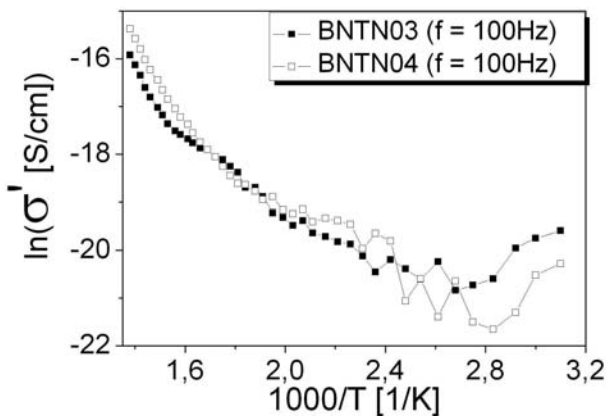
Fig. 6. The ac-conductivity dependence on reciprocal temperature for 100Hz frequency of measuring field taken under cooling for BNTN03 and BNTN04 samples

Only for elevated temperatures one can notice a straight components pointing out on thermally activated character of ac-

conductivity together with dominating contribution of dc-component. With temperature lowering the mechanism of electric charge carriers transport undergoes change. The thermal energy of ac-conductivity activation was determined for 100Hz frequency. For both samples a two approximately linear regions with two different slopes values can be separated. They are correlated with two, the same for both samples temperature ranges, namely: 723K÷653K and 643K÷553K. The energy of thermal activation values for BNTN03 equals 0.825eV and 0.319eV. Analogical values for BNTN04 equals 0.934eV and 0.592eV. The measurement uncertainty got value of 0.003eV. The collected data of ac-conductivity in the form of $\ln\sigma'_{min}(1/T)$ as a function of frequency and T_{min} for both samples are presented in the Figs. 6-7. In the case of BNTN03 sample and for frequency 10^4Hz, the temperature of $\ln\sigma'_{min}$ approaches to local maximum. At the frequency 10^6Hz, the T_{min} temperature for both samples got the same values and equals 583K.
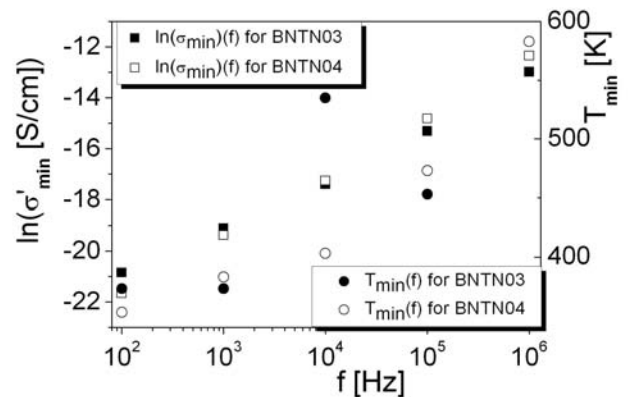
Fig. 7. The minimum values of $\ln\sigma'_{min}$ and temperatures T_{min} as a functions of measuring field frequency. Measurement was taken on cooling for BNTN03 and BNTN04 samples

4. Conclusions

In this work we check the way of preparing of $BaTiO_3$ and $NaNbO_3$ nanopowder. 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 frequency range of 20Hz÷1MHz and temperatures up to 723K. The high temperature induced dielectric dispersion in paraelectric phase as well as ac-conductivity were investigated. The energy losses within paraelectric phase were dominated by ac-conductivity. The temperature and frequency dependence of energy storage coefficient (ε') for both relaxor-type samples are similar to that described in the literature. The noticed and recorded differences, not described in the literature involve new features of relaxor behaviour in the paraelectric, high temperature range. They are correlated with samples microstructure. The thermal energy of ac-conductivity are typical for semiconductors. The data collected will be used to closer approach to high temperature paraelectric polar species modelling.

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