

Study of the relaxor behaviour in $\text{Ba}_{0.68}\text{Na}_{0.32}\text{Ti}_{0.68}\text{Nb}_{0.32}\text{O}_3$ ceramic

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Received 20.08.2009; published in revised form 01.11.2009

Properties

ABSTRACT

Purpose: The purpose of this work was to synthesize a new ceramic solid solution $\text{Ba}_{0.68}\text{Na}_{0.32}\text{Ti}_{0.68}\text{Nb}_{0.32}\text{O}_3$ (BNTN32), as well as to measure and analyse its dielectric properties within the temperature range 123 K-473 K, where dielectrically active phase transition was supposed to occur.

Design/methodology/approach: The new ceramic composition was prepared by means of conventional method. Dependence of phase transition features on temperature and frequency of measuring field were measured using dielectric spectroscopy method within the frequency range from 20 Hz to 1 MHz.

Findings: The electric susceptibility along with temperature decrease generally rises up and has transient dispersion vanishing at about 230 K. At higher and low temperatures, frequency dependence of dispersion differs in character: at temperatures at ~400 K, low frequency values dominate. Dielectric energy losses are very high at ~high temperature, they decline down while temperature decrease, and at about 200 K range its frequency dependence is reversed and less scattered with maximum at ~150 K. The whole transition of ferroelectric - paraelectric (FE - PE) type can be described by means of Curie-Weiss law and it gets diffused character.

Research limitations/implications: For modelling purposes the structure parameters of BNTN32 have to be measured by X-ray diffraction in order to establish the dielectric/structural activities of transitions taking place within used the temperature range. Additionally, dielectric measurements within broader frequency range up to 1.8 GHz will be performed.

Originality/value: The new type of ceramic material was prepared with interesting dielectric properties. Dispersion reverse of energy losses activated thermally and low frequency memory of barium titanate (BT) transition effect visible at ~400 K is to be a subject of modelling further work.

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

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

W. Bąk, Study of the relaxor behaviour in $\text{Ba}_{0.68}\text{Na}_{0.32}\text{Ti}_{0.68}\text{Nb}_{0.32}\text{O}_3$ ceramic, Journal of Achievements in Materials and Manufacturing Engineering 37/1 (2009) 24-27.

1. Introduction

Relaxors belong to a very important group of ferroelectric materials widely applied in technique [1]. It involves compounds with diffused phase transition of perovskite structures as well as those of tetragonal tungsten bronze [2]. Relaxor features are believed to be connected with a situation when more than one

type of ions occupies equivalent crystallographic position. One of the most important features of relaxors is their low frequency dispersion at maximum dielectric permittivity. The other features of this kind: Curie-Weiss law failure or dependence of phase transition temperature on the method of its determination [3]. The origin of such properties is probably connected with presence of microscopic polar regions (nano-domains) [4] in these materials.

Investigations of these materials are concentrated mainly on phase transitions [5, 6], on the domain structure [7] and on piezoeffect or pyroeffect [8]. Calorimetric and structural investigations are also sources of important information [9]. The structural investigations show that in the case of these materials only dielectric, thermally activated transition is observed without structural transition. As a model relaxor compound with perovskite structure the $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) is prepared on the lead basis [3]. At the early stage of investigations the terms applied to ferroelectrics were used. As a reason of diffusivity of phase transition, the chemical micro-heterogeneities were considered. Advances in investigations have pointed out on another reason. A new description of phase transition in PMN applies the analogy to spin glasses behaviour. L.E. Cross [3] determined PMN as super-paraelectric. It involves the existence of independent polar regions with individual dipole moments responding to the external electric field independently on each other. Recently, because of the need of environment protection new relaxor ferroelectrics have been a subject of investigation [10]. Ferroelectric solid solutions without lead prepared on the basis of BaTiO_3 (BT) and NaNbO_3 (NN) substituted in cationic sublattices by ions with different valency possess many interesting dielectric properties [11-13]. It was established that in $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_{1-x}\text{Nb}_x\text{O}_3$ for the range of admixture $0.075 \leq x \leq 0.55$ the solid solution with relaxor properties can be prepared [14, 15].

The purpose of this work was a synthesis of new solid solution ceramics: BNTN32 and investigation of its dielectric properties e.g. FE - PE phase transition features.

2. Experimental

The ceramic sample of BNTN32 was prepared by means of conventional method and BaC_2O_4 , $\text{Na}_2\text{C}_2\text{O}_4$, TiO_2 , Nb_2O_5 reagents of 99.99% purity. Reagents mixed up with ethanol were grained in a ball mill for 2 h. Next the mixture was dried up, pressed and the synthesis was initiated thermally. Temperature and time of synthesis duration was 1320 K and 15 h. Then, samples were grained again, pressed and sintered at 1420 K for 1 h. The real density of final ceramic equals 3.72 g/cm^3 . Samples in the shape of disc-pellets sized 10.0 mm (diameter) and 1.12 mm (thick) were painted using 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 applied heating and cooling agent was nitrogen. The data were taken at stabilized temperature points within the range from 473 K to 123 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 [16]. Amplitude of measured voltage was 1 V.

3. Results and discussion

The dielectric properties of BNTN32 ceramic were measured within the temperature range in which FE - PE phase transition takes place. The outcomes were recorded in the form of real and

imaginary parts of dielectric complex permittivity. Both quantities as functions of temperature and for three selected values of frequency are shown in the Fig.1. Both records point out on the diffused phase transitions of FE - PE type (relaxor type). In the case of $\epsilon'(T)$ their maximum values are shifted towards higher temperature values along with frequency increase. Values of maximums are lower for higher frequencies. Energy losses behaviour versus temperature and frequency (Fig.1), also can be qualified as typical for relaxor category. It is manifested by the fact that maximum of $\epsilon''(T)$ occurs at higher temperatures for higher frequencies. But in this case, the frequency dependence is reversed as related to $\epsilon'(T)$ behaviour at maximum. The shift of $\epsilon''(T)$ maximum at 1MHz against $\epsilon'(T)$ maximum for the same frequency amounts 30 K. This kind of behaviour is characteristic for relaxors. This type of phase transitions seems to have two basic diffusivity reasons: the first one is probably the heterogeneity of chemical composition and admixtures (presence of other chemical elements) which leads to existence of statistical distribution of Curie temperatures; the second one is the polar regions presence. In the case of investigated ceramic BNTN32, these distributions involve ions in both cationic sublattices. Additionally, dynamics and growth of polar regions are strongly temperature dependent. Thus, the external electric field applied to the sample gives the current response involving components originating from different polar regions.

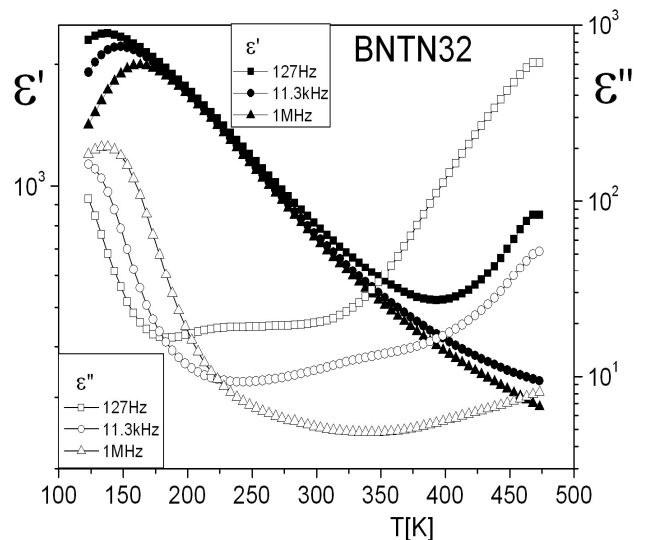


Fig. 1. The dependence of real permittivity (ϵ') and imaginary permittivity (ϵ'') at temperature for BNTN32 sample

The dependence of ϵ' on frequency for selected temperatures from paraelectric and ferroelectric phases is shown in the Fig.2. For low temperatures values of dielectric susceptibility are generally about more than two times higher and frequency dependent within the whole frequency range. At high temperature only the low frequency dispersion is visible. The energy losses dispersion for low and high temperature values are illustrated in the Fig.3. The double log-log scales were chosen to present the dispersion reverse the process induced thermally. The change from negative (high temperature) into

positive (low temperature) slopes is visible. The character of low temperature values seems to mean that the origin of energy losses is of relaxational nature rather (slope ~ -0.5) than of conductivity in phase with external electric field. The low temperature dispersion is associated with a weak relaxation for lower frequencies only. The energy absorption and dissipation expressed by real part of ac conductivity are presented in the Fig.3. This process is much weaker and temperature influence along with high to low temperature transition is associated only with small slope increase.

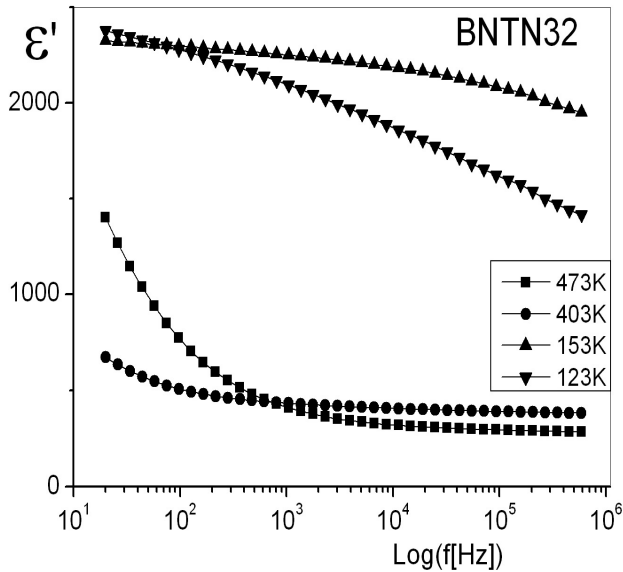


Fig. 2. Dependence of a real part of dielectric permittivity (ϵ') on frequency for BNTN32 and selected constant temperatures

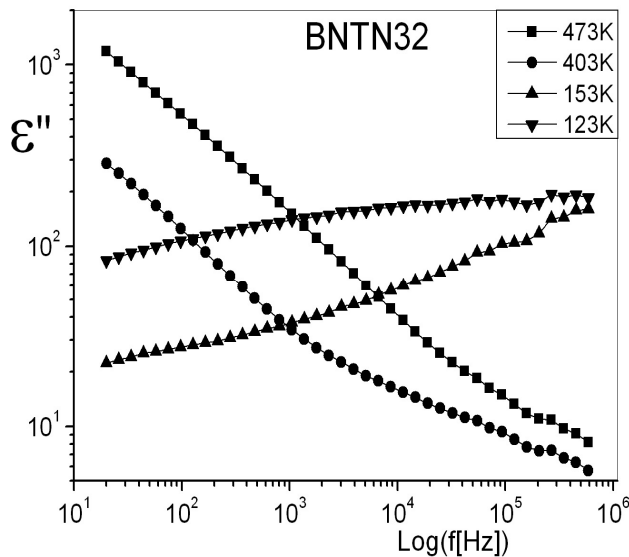


Fig. 3. Dependence of dielectric losses (ϵ'') on frequency for BNTN32 and selected constant temperatures

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

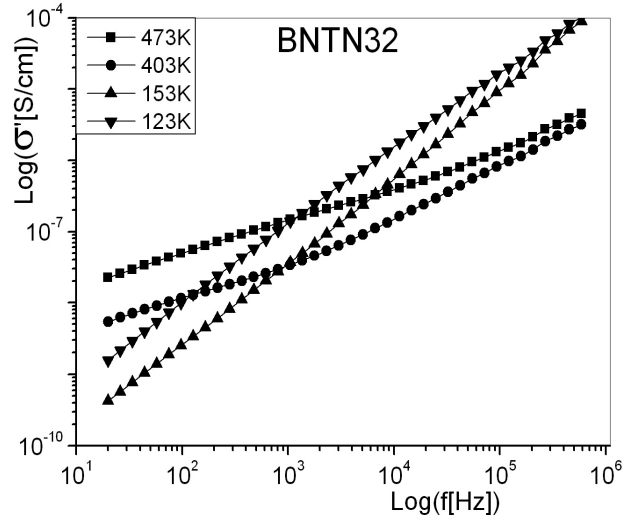


Fig. 4. The dependence of real part of ac conductivity (σ') on frequency for BNTN32 at selected constant temperatures

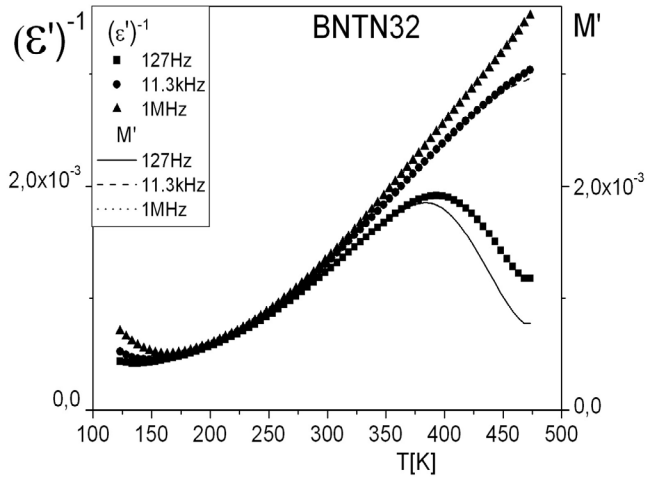


Fig. 5. The inverse of real part of dielectric permittivity ($1/\epsilon'$) and real part of electric modulus (M') as functions of temperature at chosen frequencies for BNTN32 sample

The dependence of $1/\epsilon'(T)$ and $M'(T)$ (real part of electric modulus) on temperature and selected frequencies is presented in the Fig.5. The discrepancy between both quantities visible as solid line for 127Hz and at higher temperatures points out on low frequency relaxational process domination at this temperature region. Generally, straight line fitting is possible here only for 1 MHz frequency.

4. Conclusions

Relaxor properties of the new ceramic material BNTN32 were found illustrated together with details of frequency dependence of energy losses reverse process which is thermally induced. The phase transition/evolution is strongly diffused and cannot be described by Currie-Weiss law. The nature of experimentally established features of dielectric behaviour of this new material will be a subject of further investigation.

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