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# Structural and dielectric properties of $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramics

J. Suchanicz[a,*], J. Kusz[b], H. Böhm[c], H. Duda[b], J.P. Mercurio[d], K. Konieczny[a]

[a]*Institute of Physics, Pedagogical Academy, ul.Podchorazych 2, 30-084 Krakow, Poland*
[b]*Institute of Physics, University of Silesia, ul.Uniwersytecka 4, 40-007 Katowice, Poland*
[c]*Institut fur Geowissenschaften, Johannes Gutenberg Universitat, D-55099 Mainz, Germany*
[d]*Faculte des Sciences, Universite de Limoges, 123, Av.Albert Thomas, 7060 Limoges Cedex, France*

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## Abstract

A $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramic has been studied by X-ray diffraction and by measurements of dielectric and ferroelectric properties between room temperature and 450 °C. A sharp increase in the electric permittivity and dielectric loss near 200 °C has been observed. This sharp increase in dielectric responses indicates a transformation between normal and relaxor ferroelectric states. It is found that polar regions can exist at higher temperatures. The X-ray diffraction study shows that the transformation corresponds to the first order phase transition from tetragonal to cubic. The use of the $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramic for device application has also been indicated.

*Keywords:* Actuators; Dielectric properties; (Na, Bi, Ba)$TiO_3$; Perovskites; Sintering; X-ray methods

## 1. Introduction

Since the 1970s, there has been a growing interest for mixed compositions of normal and relaxor ferroelectrics. However, the majority among these ferroelectrics are lead-based materials and so some serious problems arise in the production and treatment of such samples for device applications. Some alternative lead-free materials or such with low-lead content have been reported recently.[1–15] Some of them[1–8,13,14] are based on $Na_{0.5}Bi_{0.5}TiO_3$ (NBT).

Some properties of NBT–$BaTiO_3$ solid solutions in ceramic form for small contents of $BaTiO_3$ have been reported recently.[13,14] NBT exhibits two structural phase transition from ferroelectric rhombohedral phase to tetragonal (~200–350 °C) and to paraelectric high temperature cubic phase (520–540 °C). At about 320 °C, NBT exhibits a broad maximum of electric permittivity. This maximum does not correspond to any phase transformation but may originate from dielectric relaxation, which is suggested to be a response to electromechanical interactions between polar regions and the non-polar matrix.[16] The transformation to a ferroelectric phase at about 200 °C appears as a small broad anomaly in the electric permittivity. This anomaly exibits small relaxor characteristics. These relaxor characteristics can be improved after adding Pb[5] or Ba[6] ions to NBT. On the other hand, $BaTiO_3$ is one of the most investigated classical ferroelectric materials. At about 120 °C a phase transformation from the high-temperature cubic phase to the tetragonal ferroelectric phase takes place. The aim of the present article is to report the structural, dielectric and ferroelectric properties of a $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramic.

## 2. Experimental conditions

A conventional mixed oxide technique was used to obtain the $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramic samples in the same way as for a $Na_{0.5}Bi_{0.5}TiO_3$ ceramic;[17] a 3-step

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[*] Corresponding author. Tel.: +48-12-662-6309; fax: +48-12-637-224.

*E-mail address:* sfsuchan@ap.krakow.pl (J. Suchanicz).

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sintering process has been applied (the first two steps was the same as for pure $Na_{0.5}Bi_{0.5}TiO_3$). The conditions for the third step were as follows: 1120 °C (for 1 h) and 1200 °C (for 1.5 h). The obtained ceramics were cream-coloured, translucent, with a density greater than 95% of its theoretical value and they exhibited very good mechanical properties.

For X-ray experiments we used a Seifert powder diffractometer (XRD 3000 TT) with a high temperature device from Materials Research Instruments (mri). Measurements in air were made with Cu*K*α radiation at 45 kV and 30 mA ($\lambda = 1.5405$ A). The compound has been characterized in the $2\Theta$-range of 5–140° at room temperature. High temperature lattice parameters have been determined from diffraction patterns between 50 and 400 °C in steps of 50 °C in the $2\Theta$-range of 30–70° (steps of 0.02° in $2\Theta$, 10s/step). The structural phase transition has been recorded in the $2\Theta$-range of 43.5–48.5° in steps of 10 °C up to 270 °C (steps of 0.02° in $2\Theta$, 20s/step). The lattice parameters were calculated applying the POWDER[18] program.

The weak field (3V/cm) permittivities have been measured by using a HP 4284A LCR meter in the frequency range of 20 Hz to 1 MHz and in the temperature range of 30–450 °C. The samples were coated with silver paste or sputtered with gold. The temperature measured by a thermocouple in contact with the sample was stable within the accuracy of ±0.1 °C. Prior to electrical measurements the samples were heated at about 570 °C for 30 min to eliminate strains, both internal and at the electrode/sample interface. The data were collected regularly in steps of 3 °C on heating and cooling, with change of temperature at a constant rate and constant time for stabilisation, using an automatic system.

Pyroelectric measurements were carried out by a quasistatic method at a heating rate of 10 °C/h. Poling the sample was done by cooling from 250 °C down to room temperature in a d.c. electric field of $E = 12$ kV/cm.

Hysteresis loops were measured by the low-frequency triangular signal method using a field strength up to 45 kV/cm at a frequency of $f = 0.34$ Hz.

## 3. Results and discussion

At room temperature the sample has a perovskite simple phase with tetragonal structure and with lattice parameters $a = 3.918(3)$ Å and $c = 3.997(4)$ Å. The average grain size of the ceramic was about 3 μm. Fig. 1 presents an example of a powder diffraction pattern with a tetragonal to cubic phase transition on heating up to 270 °C and again cooling down to room temperature. The $2\Theta$ range of the 002 and 200 reflection of the tetragonal phase is exhibited in a 3-dimensional diagram. The intensity ratio of the reflections is about 1:2. On heating the 002 reflection disappears at about ~240 °C. Simultaneously the 200 reflection shows a jump in intensity and in its $2\Theta$ position. This is the tetragonal to cubic phase transition. On cooling from 270 °C there is thermal hysteresis for the reverse transformation, which is an indication for a first order phase transition. The hysteresis can be seen even better in Fig. 2, where the intensities of the pertinent reflections are exhibited. The reverse transformation occurs at about 210 °C. Fig. 3 shows the change of the lattice parameters from tetragonal to cubic,

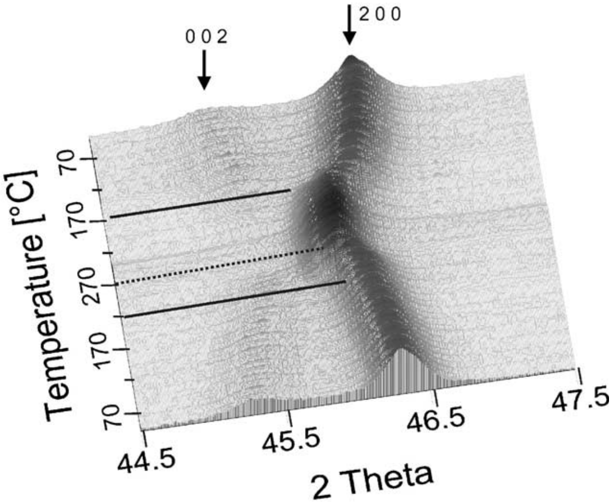

Fig. 1. Part of the powder diffraction pattern of $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ as a function of temperature and $2\Theta$ on heating and cooling.

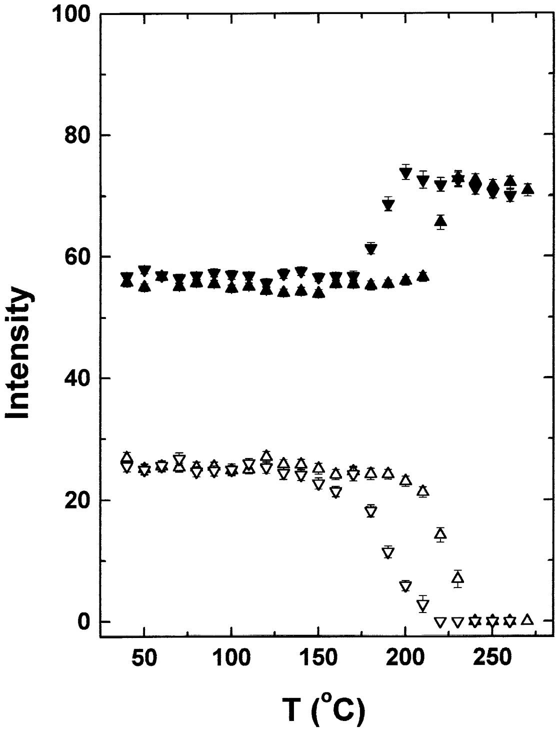

Fig. 2. The variation of the intensity of the 200 reflection (solid symbol) and the 002 reflection (open symbol) on heating (△) and cooling (▽).

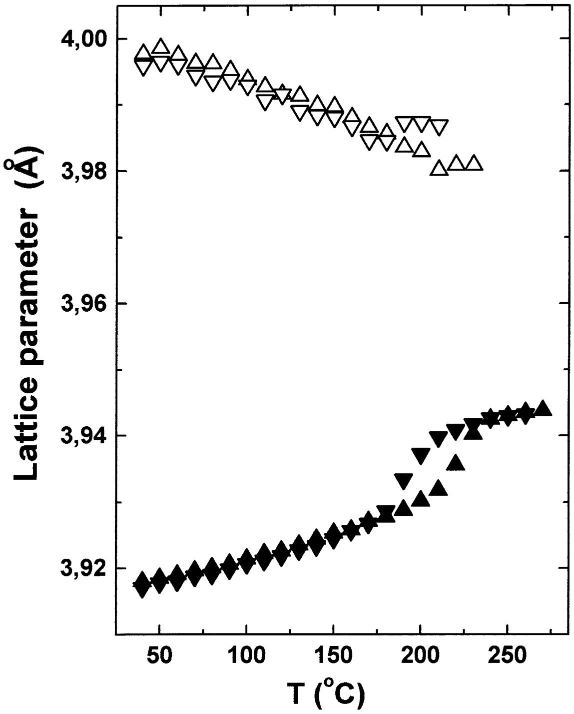

Fig. 3. The variation of the lattice parameters *a* (solid symbol) and *c* (open symbol) on heating (△) and cooling (▽).

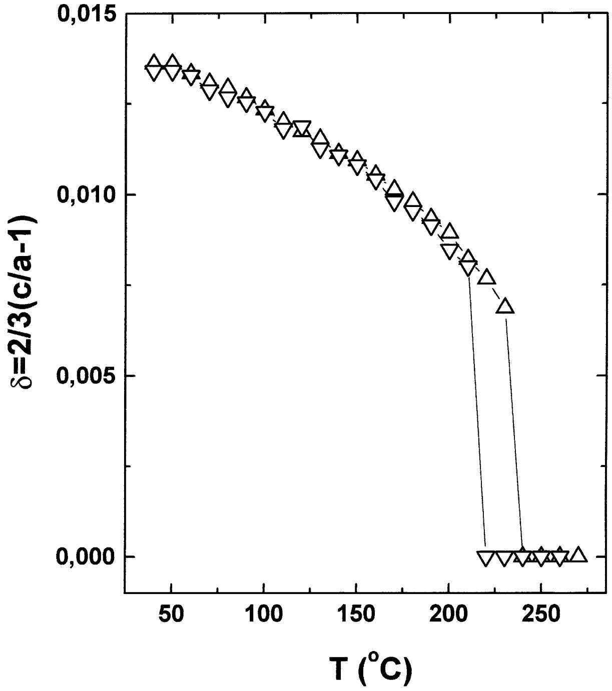

Fig. 4. The parameter $\delta$ of the spontaneous strain at the tetragonal to cubic transformation.

again hysteresis is obvious. In Fig. 4 the parameter $\delta$ (the homogeneous parameter of deformation) of the spontaneous strain at the tetragonal to cubic transformation is depicted[1]. It describes the extra strain which is associated with the transition apart from normal thermal expansion.

Figs. 5 and 6 show the temperature variation of the electric permittivity $\varepsilon$ and the dielectric loss tanδ, respectively. Obviously a cation substitution on the A-position by Ba resulted in the increase of the electric permittivity and the decrease of $T_m$ (i.e the temperature with maximal electric permittivity). Sharp increases in $\varepsilon$ and tan$\delta$ occurred on heating near 235 °C. When the sample is heated or cooled, a large thermal hysteresis (as for X-ray measurements) is observed ($\Delta T \approx 30$ °C, inserts in Figs. 5 and 6). The large thermal hysteresis is similar to that observed in first-order transitions of martensitic character. The transition temperature of tetragonal to cubic coincides with the rapid change in the $\varepsilon(T)$ curve, but not with the electric permittivity maximum. If the electric permittivity anomalies were

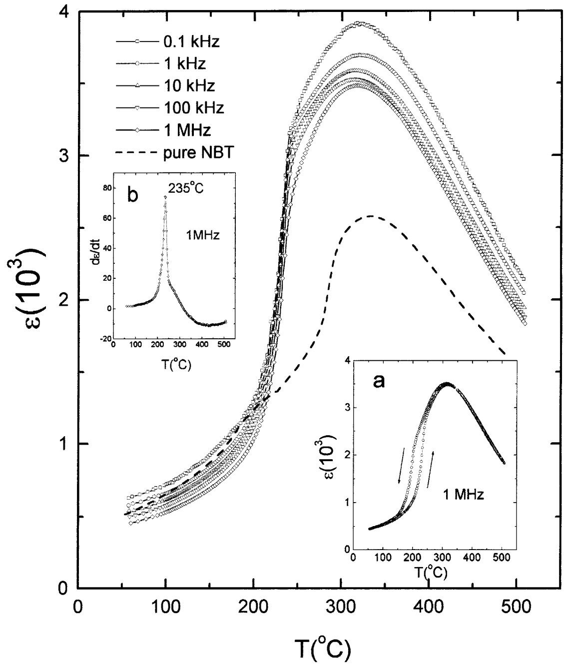

Fig. 5. Temperature/frequency dependence of the electric permittivity $\varepsilon$ of $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramic (on heating). Dashed line shows, for comparision, the temperature dependence of the electric permittivity $\varepsilon$ of $Na_{0.5}Bi_{0.5}TiO_3$ ceramic at frequency 1 kHz. The insert (a) shows the temperature dependence of electric permittivity $\varepsilon$ on heating and cooling. The insert (b) shows the temperature dependence of first derivative of the electric permittivity (on heating).

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[1] The homogeneous parameter of deformation is defined[19] by the term $\delta=(d-d_0/d_0)$, where $d$= the length of the cell in the polar axis direction, $d_0$= the length of the section adequate to $d$ (in the same direction) for the regular cell which has the same volume as the considered one. In the case of tetragonal cell we have $\delta_T \approx 2/3(c/a-1)$ while for rhombohedral one the homogeneous parameter of deformation will have the value $\delta_R \approx \cos\alpha$.

due to a normal ferroelectric phase transition of first-order, this should correspond to the transition from a tetragonal ferroelectric to a paraelectric cubic state and vice versa. However, the profile of the $\varepsilon(T)$ anomaly in Fig. 5 is different from a normal ferroelectric phase transition, i.e. after an abrupt jump in the $\varepsilon(T)$-curve there is a "diffuse region". The temperature $T_D$, at which the "diffuse region" of the electric permittivity begins, depends on the frequency. This temperature, namely, is shifted toward high temperature with increasing frequency (Fig. 5). In addition the value of the electric permittivity decreases with increasing frequency. Simultanously the values of tanδ increase and the temperature of its maximum is shifted to higher temperature with increasing frequency (Fig. 6). Thus the dielectric responses in the temperature $T_D$ show a typical relaxor behaviour. This relaxor behaviour is more effective than for pure NBT. The dielectric behaviour indicates a transformation between a normal and a relaxor ferroelectric state in our material. It can therefore be suggested that the tetragonal to cubic transition should be divided into two parts. One part exhibits the abrupt increase of the electric permittivity, it is associated with the structural change of a first order phase transition and the characteristic hysteresies. The second part is a "diffuse" part associated with small tetragonal (polar) regions existing in a matrix of cubic symmetry. Such small regions of the low-temperature ferroelectric phase exist already at temperatures far above $T_m$. In this temperature range there are unstable fluctuations which do not interact. With decreasing temperature these regions grow and start interacting and are expected to become the nuclei of low-temperature ferroelectric phase. The pyroelectric and hysteresis loop measurements tend to support this assumption (see later). The local tetragonal regions are small and have random orientations of the tetragonal axis with respect of the three equivalent cubic directions yielding an average cubic symmetry. From this point of view, the maximum of the electric permittivity may originate from relaxation processes connected with both electrical and mechanical interactions between polar regions and the non-polar matrix, as for pure NBT. The shifts of the temperature $T_m$ as a function of frequency characteristic for relaxors cannot be observed, like for pure NBT (Fig. 5).

The temperature dependence of the remanent polarization obtained from pyroelectric measurements is shown in Fig. 7. It can be seen that Ba (30% mol) doping causes the increase of the remanent polarization. The fastest changes of the remanent polarization appear in the temperature range where structural phase transition occurs (Figs. 1–4) and rapid change of the electric permittivities can be observed (Figs. 5 and 6). It should be noted that the remanent polarization remains non-zero up to about 260 °C, which can be an indication for the existence of polar regions at higher temperatures (at about 240 °C structural phase transition occurs).

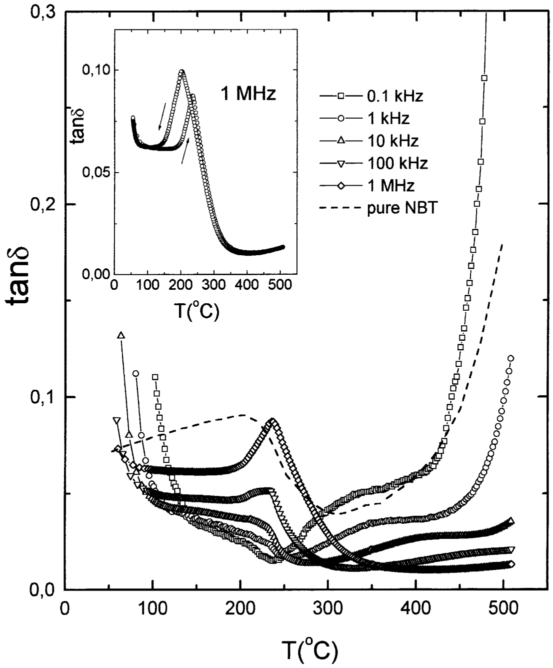

Fig. 6. Temperature/frequency dependence of the dielectric loss tanδ of $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramic. Dashed line shows, for comparison, the temperature dependence of the dielectric loss tanδ of $Na_{0.5}Bi_{0.5}TiO_3$ ceramic at frequency 1 kHz. The insert shows the temperature dependence of the dielectric loss tanδ on heating and cooling.

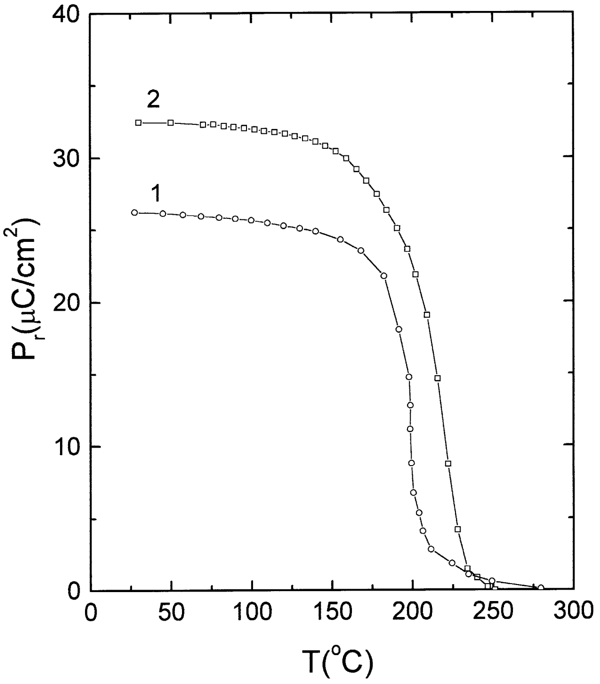

Fig. 7. Temperature dependence of the remanent polarization of $Na_{0.5}Bi_{0.5}TiO_3$ (1) and $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ (2) ceramics.

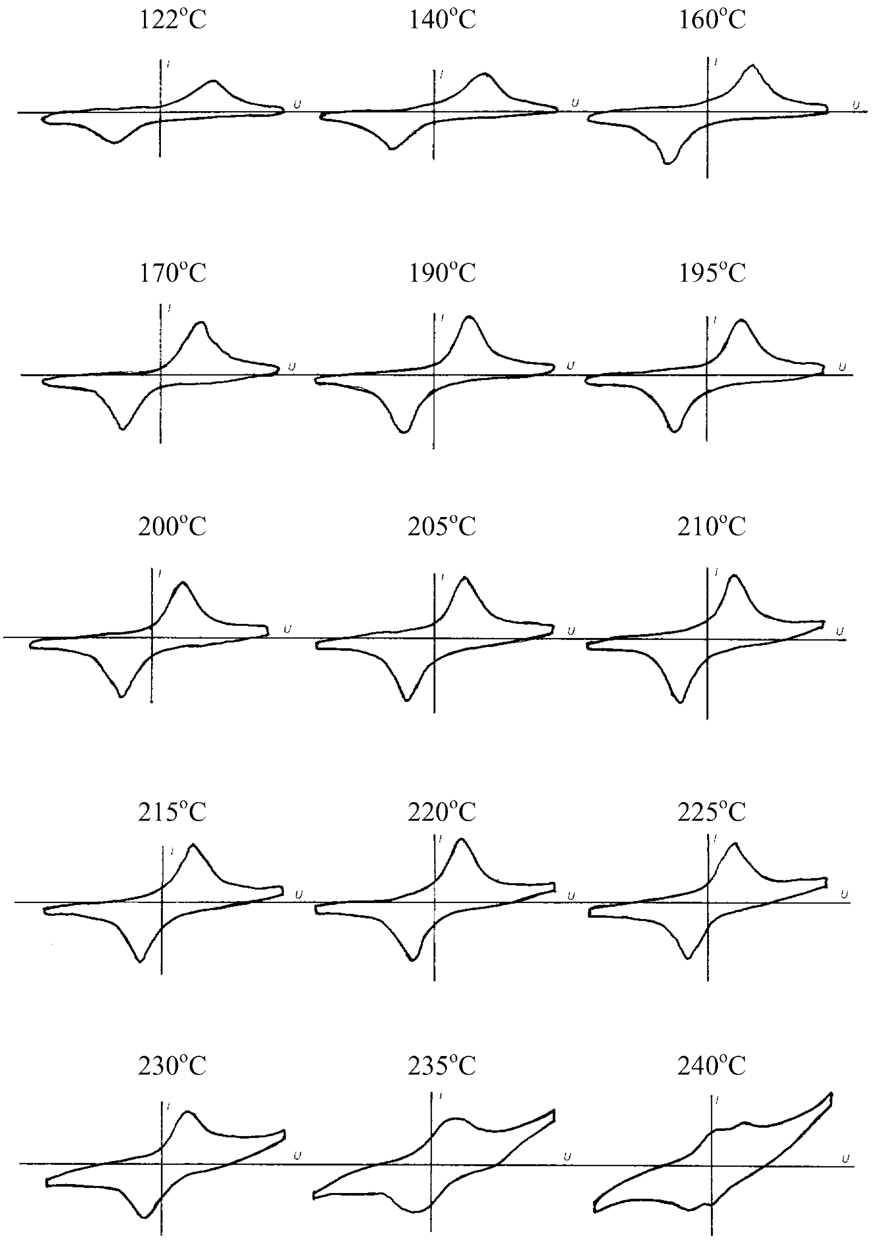

Fig. 8. Examples of current hysteresis loops of $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ ceramic.

Examples of hyseresis loops obtained by the low-frequency triangular signal method are shown in Fig. 8. It is seen that up to a temperature of ~230 °C the shape of the hysteresis loops is typical for a ferroelectric phase. For temperatures above about 230 °C these loops do not disappear but are deformed. Deformed hysteresis loops are typical for coexisting phases (polar and macroscopically non-polar phases).[16,20] The occurence of these loops are the evidence of non-stabilities of local phase transitions induced by a strong electric field.[16] The deformed hysteresis loops observed in our material can be the indication for coexisting phases (tetragonal polar regions in a non-polar cubic matrix).

## 4. Conclusions

A lead-free ceramic sample of $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ is favourable because by its use the environment is less polluted. The structure, dielectric, pyroelectric and ferroelectric properties for this sample have been measured. Analysing the results of these measurements we conclude that: (i) the material has tetragonal symmetry at room temperature and undergoes a first-order tetragonal to cubic phase transformation between 210 and 240 °C. It is concluded from measurements of dielectric and ferroelectric properties, that this transformation is a transition between a normal and a relaxor ferroelectric state, (ii) incorporation of Ba cations (30% mol) in

$Na_{0.5}Bi_{0.5}TiO_3$ improves its dielectric (also relaxor) and ferroelectric properties, (iii) it should be expected that in the range of a morphotrophic phase boundary these properties will further be improved, because ferroelectrics usually have the best electromechanical properties in morphotropic phase boundaries. This could make this material interesting for future applications (electronic ceramic as dielectrics for capacitors, actuators, displacement transducers, and micro-electromechanical system-based applications).

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