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Dielectric properties of $(Na_{0.5}Bi_{0.5})_{1-x}Me_xTiO_3$ ceramics near morphotropic phase boundary

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Ceramic samples of modified ferroelectric sodium-bismuth titanate $(Na_{0.5}Bi_{0.5})_{0.87}$ $Me_{0.13}TiO_3$ (Me = Pb, Sr and Pb + Sr), were prepared using conventional solid state reaction techniques. The studies of powder X-ray diffraction of the obtained compounds revealed their rhombohedral symmetry at room temperature, the increase of lattice constant and the increase of rhombohedral lattice distortion (except for the material with Sr dopand, where distortion decreases). Temperature (at room temperature to 400°C) and frequency (at 20 Hz to 1 MHz) dielectric measurements reveal that A-site cations addition of Pb and/or Sr have resulted in the increase of relative electric permittivity. However, the temperature T_m (when the electric permittivity is a maximum) increases after Pb or Sr doping and it decreases after (Pb + Sr) doping.The pyroelectric and current loop measurements have shown that all samples were ferroelectric. The results of these measurements also allowed us to determine the temperature variation of the remanent and spontanous polarizations. The polarizations are found to decrease after Pb or Sr doping and increase after (Pb + Sr) doping. The piezoelectric constants (d_{33} and d_{31}) and electromechanical coupling factors (k_{33} and k_{31}) were obtained from resonance-antiresonance measurements method. The best piezoelectric and electromechanical properties have NBT doped by Pb. This ceramic may be good candidate for device applications. The diffuse ferroelectric phase transition of the investigated materials, similarly as for pure NBT, has been revealed. The properties of these materials (especially in diffuse phase transition range) can be explained by the behaviour of polar regions.

1. Introduction

The PZT-ceramics and its modifications are fundamental materials used for constructing of piezoelements. Good piezoelectric properties of this material are connected with the occurrence of morphotropic phase boundary (MPB). However, it is difficult to obtain the desired composition due to of great volatility of lead (Pb). In the process of obtaining of this material it is necessary to maintain the atmosphere enriched with the vapor of lead oxide (PbO). Compositions with low-lead and free from lead could be of great interest for applications.

Some new piezoelectric materials based on sodium-bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) have been recently discovered, as it has been mentioned in papers [1–8]. In contrast to PZT, these materials can be obtained in normal atmospheric conditions. In system $(Na_{0.5}Bi_{0.5})_{1-x}Me_xTiO_3$, where:Me = Cd, Ba, Ca,......, the MPB exists for $0.12 < x < 0.14$ ($x = 0.06$ for Ba). These solid solutions seems to be attractive piezoelectric and pyroelectric materials.

NBT has a perovskite structure and a rhombohedral symmetry with ferroelectric properties below a temperature of about 200 °C. In the temperature range 540 °C to 520 °C a phase transition between cubic and tetragonal phases occurs. The maximum of electric permittivity occurs at about $T_m \approx 320$ °C. Simultanously no changes in crystal structure, domain structure, specific heat etc are observed about this temperature. A strong diffuse phase transition between tetragonal and rhombohedral phases takes place in NBT in a wide temperature range (including T_m) in which both phases coexist [9–11]. It follows, from neutron scattering measurements that already at high temperatures (above T_m) the unstable polar regions arise [12]. Their correlation radius increases with the decrease of temperature and below the temperature of 280 °C these regions are stable. They act as the nucleation centers of the ferroelectric state which occur below about 200 °C. Taking into account the neutron scattering and another results of measurements, the anomalies of some quantities (electric permittivity, electrostrictive strain, pyroelectric coefficient etc.), which appear in vicinity of 320 °C, should be associated with relaxation processes, which originate from electromechanical interacting between polar regions and nonpolar matrix [13, 14].

In the literature there is scant information concerning the properties of $(Na_{0.5}Bi_{0.5})_{1-x}Me_xTiO_3$. Morever there are controversies concerning the range of x-values, for which the MPB exists in this system. In the present paper, measurements of the structural, dielectric, piezoelectric and ferroelectric properties of $(Na_{0.5}Bi_{0.5})_{0.87}Me_{0.13}TiO_3$ ceramics for Me = Pb or Sr and (0.5Pb + 0.5Sr) have been undertaken. It has been also idicated for the possibility of applications of this family of ferroelectrics.

2. Experimental details

2.1. Preparation of the samples

Ceramic samples were obtained by the conventional solid state reaction method in the same way as in case of NBT ceramics [15]. The following ceramics have been prepared: $(Na_{0.5}Bi_{0.5})_{0.87}Pb_{0.13}TiO_3$, $(Na_{0.5}Bi_{0.5})_{0.87}Sr_{0.13}TiO_3$ and $(Na_{0.5}Bi_{0.5})_{0.87}(0.5\,Pb + 0.5Sr)_{0.13}TiO_3$. Three successive sinterings in closed corrundum crucible were carried out, i.e. at 700 °C–800 °C, next in the temperature range 900 °C–1100 °C, and again at the temperature of about 1200 °C–1300 °C. Thus the firing temperature is more than 100°C lower that for PZT. Ceramics obtained in these technological conditions were cream-coloured, small porosity, with density greater than 95% of theoretical density and exhibited very good mechanical properties.

2.2. X-ray diffraction measurements

X-ray diffraction measurements were performed by a modified DRON 1.5 diffractometer and controlled by IBM computer. The Cu K_α radiation was filtered. The powdered ceramics were investigated. The samples were pre-heated in the temperature 600 °C for a half an hour. The temperature was stabilized with the accuracy equal to ±0.1 °C.

2.3. Dielectric measurements

The weak field (3V/cm) dielectric measurements were made using HP 4284A LCR meter for the frequency range 20 Hz to 1 MHz and for the temperature range 30 °C to 400 °C. The samples were previously electroded by silver paste or sputtered with gold. The temperature of samples was controlled by a thermocouple with the accuracy of ±0.1 °C. Before experiments the samples were heated for at least 0.5 hour at about 570 °C to release any strains both internal and those at the electrode/sample interface. The temperature dependence of permittivities was measured while the temperature of the samples was increasing or decreasing at a rate of 100 °C /hour.

2.4. Polarization measurements

The remanent and spontanous polarizations were obtained from pyroelectric and from current loops measurements, respectively. Pyroelectric measurements were performed in quasistatic method on heating. In this case, ceramics were preliminary polarized in the d.c. electric field strength up to 22 kV/cm applied at about 250 °C and switched off at room temperature. In the second case the method of low-frequency triangular signals described in paper [16] has been used. Such measurements were performed for the electric field strength up to 55 kV/cm and frequency 0.025 Hz. Under these experimental conditions the saturation state was achieved.

3. Results and discussion

At room temperature, NBT has rhombohedral symmetry, whereas $PbTiO_3$ has tetragonal symmetry. On the other hand $SrTiO_3$ has cubic symmetry at room temperature. Therefore, a MPB in NBT-based solid solutions, with respect to composition, can be expected to exist at room temperature. For $(Na_{0.5}Bi_{0.5})_{1-x}Pb_xTiO_3$ system, MPB at $x = 0.13$–0.15 [4] and at $x = 0.26$ for $(Na_{0.5}Bi_{0.5})_{1-x}Sr_xTiO_3$ system [7], have been found.

All samples reported in the present paper, similar to undoped NBT, have rhombohedral symmetry at room temperature. The space group R3c have been postulated. Substitution of Pb and/or Sr cations (13% mol) to NBT has provided the increase of lattice constant at room temperature (Table I). Also the increase of rhombohedral lattice distortion (except for 13% mol

TABLE I Lattice constants, rhombohedral distortions, polarizations, piezoelectric constants and electromechanical coupling factors of $(Na_{0.5}Bi_{0.5})_{0.87}\,Me_{0.13}TiO_3$ at room temperature

Material	Lattice constant (Å)	Rhombohedral distortion (90°-α)	Polarization (P_r, $\mu C/cm^2$)	Polarization (P_s, $\mu C/cm^2$)	d_{33} (pC/N)	d_{31} (pC/N)	k_{33}(%)	k_{31}(%)
$(Na_{0.5}Bi_{0.5})TiO_3$	3.886 ± 0.003	0.40	27	30	74	29	44	21
$(Na_{0.5}Bi_{0.5})_{0.87}Sr_{0.13}TiO_3$	3.894 ± 0.003	0.30	7	8	19	10	19	12
$(Na_{0.5}Bi_{0.5})_{0.87}Pb_{0.13}TiO_3$	3.902 ± 0.003	0.54	19	21	89	30	52	20
$(Na_{0.5}Bi_{0.5})_{0.87}(0.5\,Pb + 0.5Sr)_{0.13}TiO_3$	3.904 ± 0.003	0.53	38	42	37	28	44	30

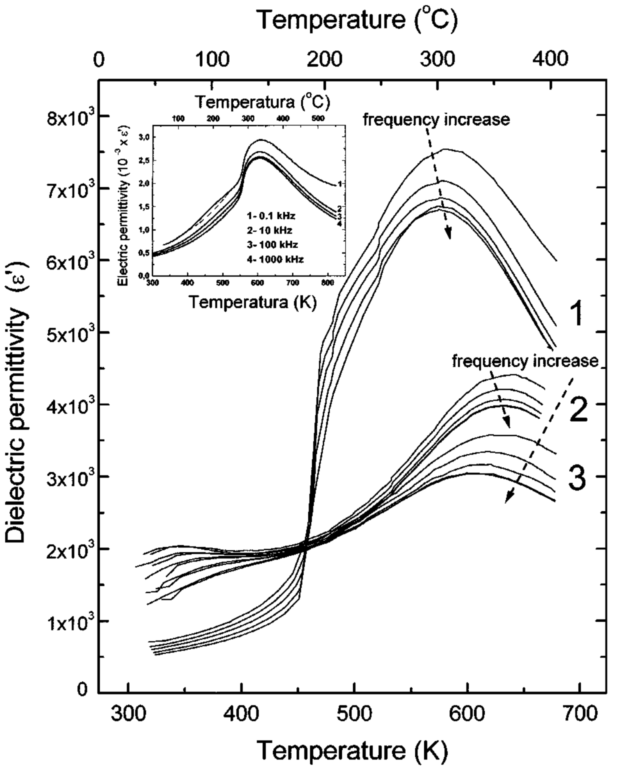

Figure 1 Temperature dependence of the electric permittivity ε' of $(Na_{0.5}Bi_{0.5})_{0.87}Me_{0.13}TiO_3$ at frequencies of 0.1, 1, 10, 100 and 1000 kHz for Me = (Pb + Sr) (1), Me = Pb (2) and Me = Sr (3) on cooling. Insert shows, for comparision, the temperature dependence of electric permittivity ε' for pure NBT [15]. The dashed line below the $\varepsilon'(T)$ curve (for frequency 0.1 kHz) in insert is draw to show the bump near 200 °C.

Sr substitution, where distortion decrease - Table I). These results are in fully accordance with the recently reported data [4, 7].

The temperature/frequency dependence of the electric permittivity ε' and the dissipation factor tanδ are shown in Figs 1 and 2, respectively. The dissipation factor tanδ for pure NBT (Fig. 2-dashed lines) is shown only for one frequency (1 kHz) in order to make the graph distinguishable. Comparing data from Figs 1 and 2 with the results for pure NBT one can notice that:

(i) relative electric permittivity increases after Pb and/or Sr doping of NBT.

(ii) the temperature T_m, in which the maximum value of electric permittivity appears, decreases after (Pb + Sr) doping of NBT. However after dopping by Sr or Pb, T_m slightly increases.

(iii) the bump in the electric permittivity, which for pure NBT occurs near 200 °C (insert in Fig. 1) [17] and is related to the formation of the ferroelectric phase, is transformed to local broad maximum and shifts to about 80 °C (at 1 kHz) after Pb or Sr doping. This local broad maximum seems to have relaxor character. Namely the value of electric permittivity in this maximum decreases and its temperature is shifted upward with frequency.

(iv) for sample with (Pb + Sr) dopping in the place of bump (near 200 °C) there is a fast increase of electric permittivity. After this fast increase of electric permittivity there is a "diffuse region". The similar sharp increase of electric permittivity, but at about 280 °C (insert in Fig. 1), was observed for pure NBT and is

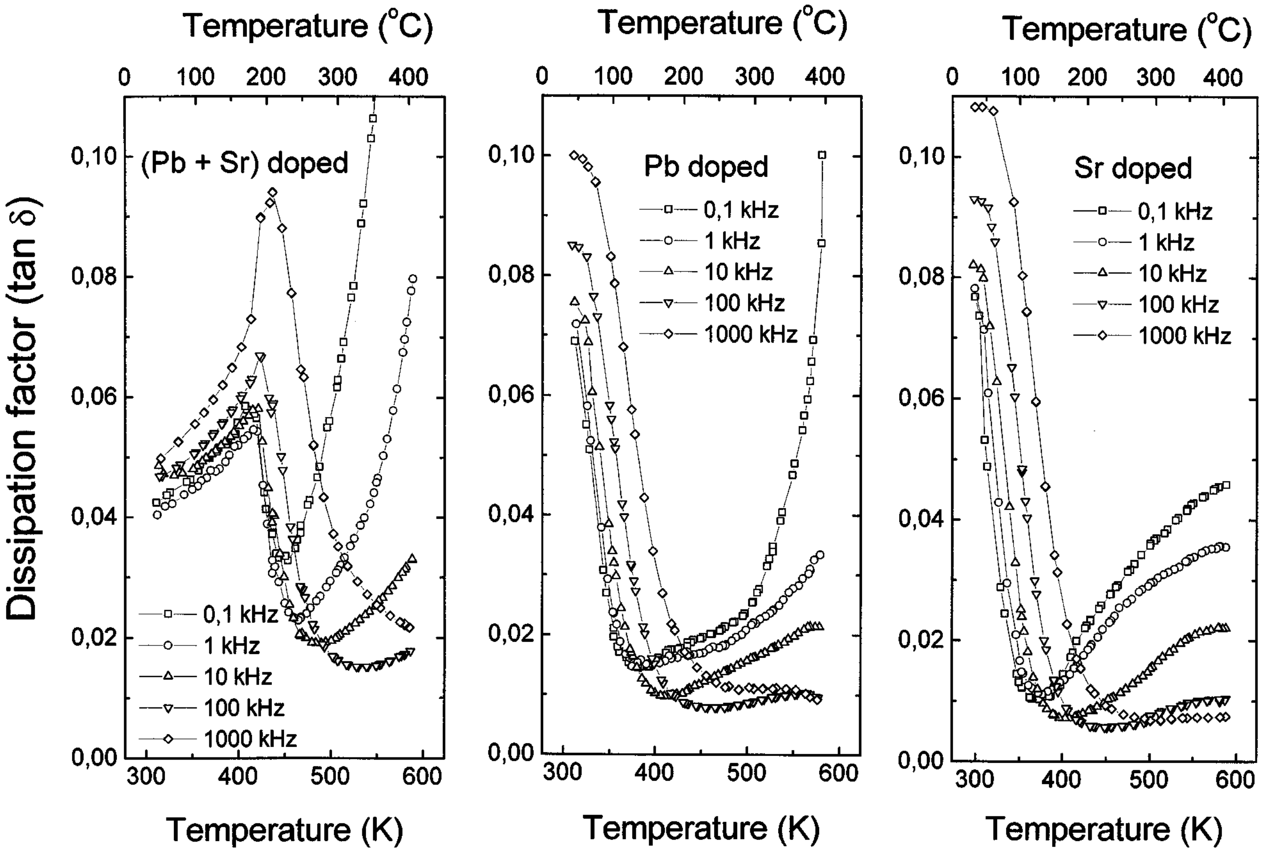

Figure 2 Temperature dependence of the dissipation factor tanδ of $(Na_{0.5}Bi_{0.5})_{0.87}$ $Me_{0.13}TiO_3$ on cooling.

connected with fast phase transition rate from the rhombohedral phase to the tetragonal phase [17]. The same situation we can expect for (Pb + Sr) doping of NBT.

(vi) after (Pb + Sr) doping, dielectric losses tanδ are similar to pure NBT. Only local maximum at about 200°C, which for pure NBT is diffuse, after doping is more sharp.

(vii) After Pb or Sr doping, local maximum in tanδ, which for pure NBT appears at about 200 °C, is shifted to temperatures below room temperature. Also the value of tan(in this maximum seems to be larger.

Pb or Sr doping of NBT provides the decrease of remanent polarization and its disappearance at lower temperature (Fig. 3 and Table I). Simultaneously rhombohedral lattice distortion for Sr dopping decreases but for Pb doping it increases. On the contrary, (Pb + Sr) doping causes the increase of remanent polarization and its disappearance at higher temperature and the increase of lattice distortion (Fig. 3 and Table I). The hysteresis loops obtained by low-frequency triangular signals were typical for ferroelectric state for all measured samples. The spontaneous polarization P_S obtained from these measurements was about 10–13% larger than the remanent polarization P_r obtained from pyroelectric measurements. The values of P_S at room temperature are shown in Table I. When the temperature increases the hysteresis loops are deformed (above 80 °C for Sr doping, above 90 °C for Pb doping and above 215 °C for (Pb + Sr) dopping). Also for pure NBT deformed hysteresis loops but above 200 °C have been obtained [14]. In NBT the presence of the deformed hysteresis loops seems to be connected just with the coexistence of phases with different symmetry (rhombohedral polar regions in nonpolar tetragonal matrix) and would be the evidence of nonstabilities of local phase transitions induced by strong electric field [14]. Electric field both deforms and reverses the polar regions, which (due to their elastic properties) do not come back to their initial shapes. In these case, the investigated sample behaves as if it was under the permanent resultant mechanical stress [14]. The similar situation is expected for our all materials. Indeed, the existence of polar regions in NBT-based solid solutions (in NBT doped by Pb [5]) and nonuniform polarized islands (in NBT doped by Sr [7]) have been postulated.

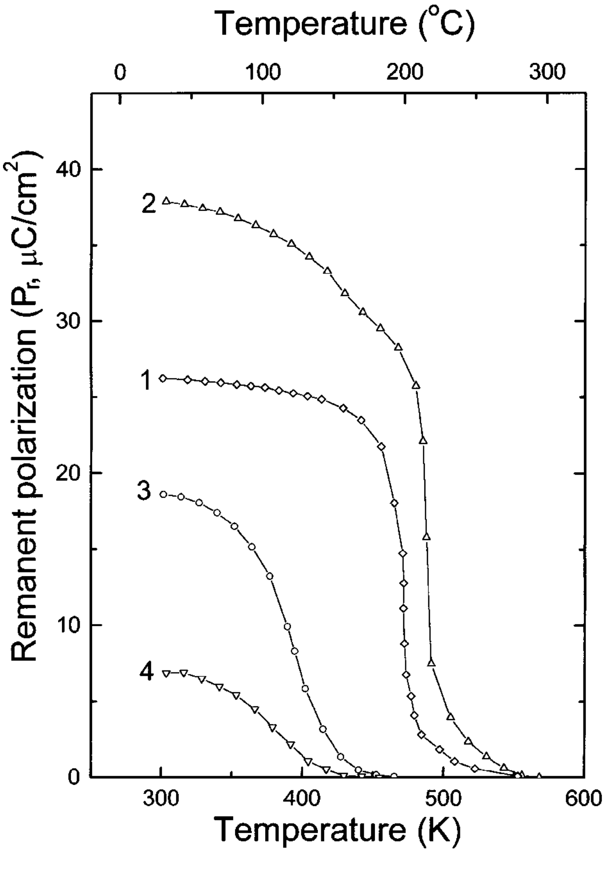

Figure 3 Temperature dependence of the remanent polarization of NBT (1) and $(Na_{0.5}Bi_{0.5})_{0.87}Me_{0.13}TiO_3$ for Me = (Pb + Sr) (2), Me = Pb (3) and Me = Sr (4).

The doping of NBT by Pb leads to the improvement of its piezoelectric and electromechanical properties (Table I). However the doping of NBT by Sr or (Sr + Pb) makes these properties worse (Table I).

The values of electronegativites (according to Pauling scale) indicate to similar character of sodium and strontium, and lead and bismuth bonding (i.e.ionic-covalent bond). On the other hand the values of ionic radius of these ions differ slightly (from 0.95 Å for Na^{+1} and 1.13 Å for Sr^{+2}). For this reason it can be expected that the difference in values of ionic radius cannot disturb the structure the above mentioned impurities) have the polarizability of individual ions. The above problem of determination of dependencies between composition-structure and properties requires many different studies both experimental and theorethical.

It seems, that the NBT-based materials reported in the present paper, have similar to pure NBT diffuse ferroelectric phase transition. These materials did not show the typical for relaxor ferroelectrics T_m-shift as a function of frequency, like for undoped NBT. From $\varepsilon'(T)$ run, we can conclude, that diffuse phase transition for Pb or Sr doping begins on cooling at about of 320 °C (where main maximum of ε' occurs) and it stops at about of 80 °C (where local maximum of ε' of relaxor character occurs). In the temperature range among these maxima the polar regions in non-polar matrix exist. Electromechanical interactions of these polar regions and non-polar matrix have delivered dielectric dispersion and leads to the existence of the deformed hysteresis loops. Below temperature about 80 °C the hysteresis loops were typical for ferroelectric state, what can be the evidence that below this temperature a rapid growth of ferroelectric ordering takes place. For NBT doped by (Pb + Sr) the diffuse ferroelectric phase transition stops at about 200 °C, where sharp decrease of ε' is observed. The main maximum of ε' for the investigated materials can be connected with the dynamic effect due to relaxation processes, which could be associated with the response of interactions (both electrical and mechanical nature) of polar regions and non-polar matrix, similar to pure NBT. Further detail studies are needed. These studies are in progress.

4. Conclusions

Ceramic samples of NBT-based materials with low-lead and free from lead favourable in the way of the environmental protection were prepared. The structure, dielectric, pyroelectric, hysteresis loops and piezoelectric data for these samples were reported. Analyzing these data we conclude that:

(1) all investigated materials have rhombohedral symmetry and are ferroelectric at room temperature like the pure NBT,

(2) substitution of Pb or Sr cations (13% mol) to NBT provides the decrease of the existence of ferroelectric state and the decrease of the value of polarization. However, (Pb + Sr) doping (13% mol) provides the increase of the existence of ferroelectric state and the increase of the value of polarization,

(3) the substitution of Pb (13% mol) to NBT provides the improvement of its piezoelectric and electromechanical properties. It should be expected that in the range of MPB these properties undergo the futher improvement, what can make this material very interesting for applications (electronic ceramics as dielectrics for capacitors, acturators, displacement transducers and microelectromechanical systems-based applications),

(4) investigated materials seems to have the diffuse ferroelectric phase transition similar as the pure NBT with wide region of phase coexistence (polar regions in non-polar matrix).

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