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Structural and electric properties of $(Na_{0.5}Bi_{0.5})_{0.88}Ba_{0.12}TiO_3$

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Abstract Lead-free $(Na_{0.5}Bi_{0.5})_{0.88}Ba_{0.12}TiO_3$ ceramics have been prepared and studied by X-ray diffraction and by the complex dielectric response as a function of temperature, frequency and a.c. field intensity. Relaxor-like dielectric behaviour were induced by barium Ba dopping to $Na_{0.5}Bi_{0.5}TiO_3$. It was shown, that relaxor-like characteristics can be enhanced by the increase of the a.c. field intensity. A sharp increase in the electric permittivity and dielectric loss on heating near 230 °C has been observed. This sharp increase in dielectric responses indicates a transformation between classical and relaxor ferroelectric phases. The X-ray diffraction study shows that this transformation corresponds to the first order phase transition from tetragonal to cubic. The use of $(Na_{0.5}Bi_{0.5})_{0.88}Ba_{0.12}TiO_3$ ceramics for device applications has been indicated.

Introduction

Relaxor ferroelectric materials are technologically important and have been widely investigated. In perovskite materials, the relaxor behaviour occurs dominantly in lead-based compositions. However the lead compounds are toxic and the high volatileness of PbO causes compositional inhomogeneities and the formation of the unwanted pyrochlore phase. In the process of producing these materials it is necessary to maintain the atmosphere enriched with the vapour of lead oxide (PbO). Therefore the search for lead-free materials are important.

Some low-lead content and lead-free materials, including the $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and NBT-based solid solutions yield excellent properties and could be good candidates for replacing materials based on lead [1–13]. In contrary to lead-based compositions, NBT–$BaTiO_3$ (NBT-BT) materials can be obtained in normal atmospheric conditions. Some properties of NBT-BT system for low [14–19] and for high [20–22] contents of BT have been reported recently. It was shown that relaxor-like behaviour can be induced by Ba doping to NBT [14–22].

NBT exhibits two structural phase transitions from a ferroelectric rhombohedral phase to a tetragonal (~260–350 °C) and further on to a paraelectric high temperature cubic phase (520–540 °C). At about 320 °C, NBT exhibits a broad maximum of the 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 [23]. The shift of temperature T_m (i.e. the temperature with maximal electric permittivity) with respect to frequency, typical for relaxors, was not observed. The relaxor-like characteristics can be induced 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.

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The aim of this work is to examine the structural, dielectric and ferroelectric properties of $(Na_{0.5}Bi_{0.5})_{0.88}Ba_{0.12}TiO_3$ (NBTB12) ceramics.

Experimental conditions

A conventional mixed oxide technique was used to obtain the $(Na_{0.5}Bi_{0.5})_{0.88}Ba_{0.12}TiO_3$ ceramic samples in the same way as for a $Na_{0.5}Bi_{0.5}TiO_3$ ceramics [24]. A 3-step sintering process has been applied (the first two steps were the same as for pure $Na_{0.5}Bi_{0.5}TiO_3$) . The conditions for the third step were as follows: 1,110 °C (for 1 h) and 1,180 °C (for 1.5 h). The obtained ceramics was cream-coloured, translucent, with a density greater than 95% of its theoretical value and it 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 (λ = 1.5405 Å). The compound was characterized in the 2Θ-range of 5–140° at room temperature. The lattice parameters were calculated applying the POWDER [25] program. The structural phase transition has been recorded in the 2Θ-range of 43.5–48.5° in steps of 10 °C up to 270 °C (steps of 0.02° in 2Θ, 20 s/step). A high temperature change of lattice parameters has been determined from the diffraction of the (2 0 0) and the (0 0 2) reflections.

The 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 a temperature change at a constant rate and constant time for stabilization, using an automatic controller.

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

Results and discussion

At room temperature the structure is tetragonal with lattice parameters a = 3.902(1) Å and c = 3.965(1) Å. Figure 1 presents diagram of a powder diffraction pattern with the tetragonal to cubic phase transition on heating up to 270 °C and further cooling down to room temperature. The ranges of temperature and of 2Θ of the (0 0 2) and (2 0 0) reflections of the tetragonal phase are exhibited in a 3-dimensional plot. On heating the (0 0 2) reflection disappears at about 220 °C. Simultaneously the (2 0 0)

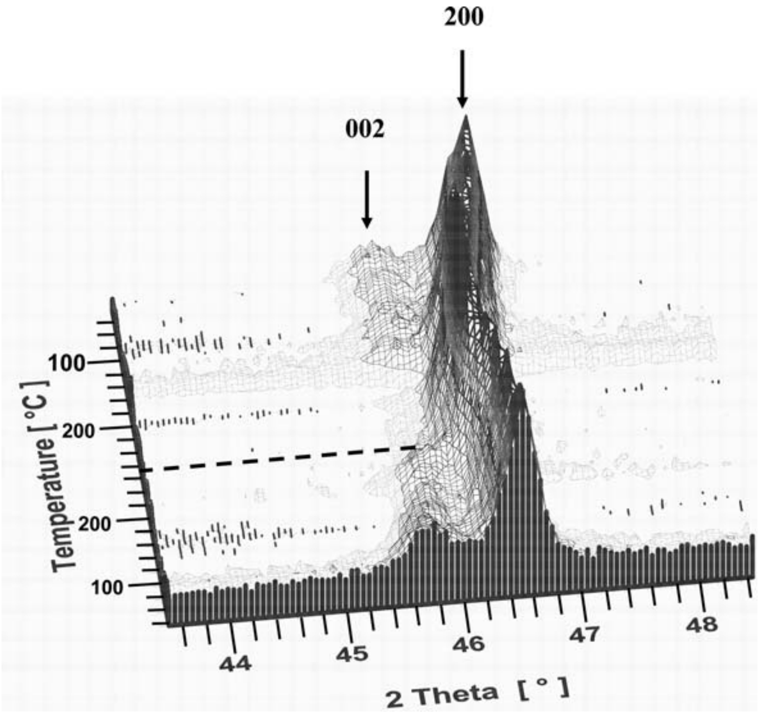

Fig. 1 Part of the powder diffraction pattern of the $(Na_{0.5}Bi_{0.5})_{0.88}Ba_{0.12}TiO_3$ as a function of temperature and 2Θ on heating and cooling

reflection shows a jump in intensity (Fig. 2) and in its 2Θ position. On cooling from 270 °C there is a thermal hysteresis for the reverse transformation which is an indication for a first order phase transition. The reverse transformation occur at about 190 °C. Figure 3 shows the change of the lattice parameters from tetragonal to cubic, again a hysteresis is observed. In Fig. 4 the parameter Δ of the spontaneous strain at the tetragonal to cubic transformation (on heating) and from the cubic to tetragonal transformation (on cooling) is depicted. It describes the extra strain which is associated with the transition apart from normal thermal expansion [26].

Figure 5 shows the temperature/frequency dependence of the weak-field (0.01 kV/cm) electric permittivity ε and the dielectric loss $\tan\delta$. Comparing this figure with data for NBT we conclude, that the contents of Ba resulted in larger ε about T_m and reductions in $\tan\delta$. Moreover, NBTB12 ceramics possess relaxor-like behaviour, including shifts of T_m with increased frequency. When the sample is heated and cooled, a large thermal hysteresis (as for the X-ray data) is observed ($\Delta T \approx 30$ °C, inset in Fig. 5) indicating a first order phase transition. Sharp increases in electric permittivity and dielectric loss occurred on heating at about 230 °C (Fig. 5). This sudden increase in dielectric response coincides with the tetragonal to cubic phase transition (see X-ray data). These data are very similar to the results obtained for $(Na_{0.5}Bi_{0.5})_{0.70}Ba_{0.30}TiO_3$ [16] and $(Na_{0.5}Bi_{0.5})_{0.50}Ba_{0.50}$

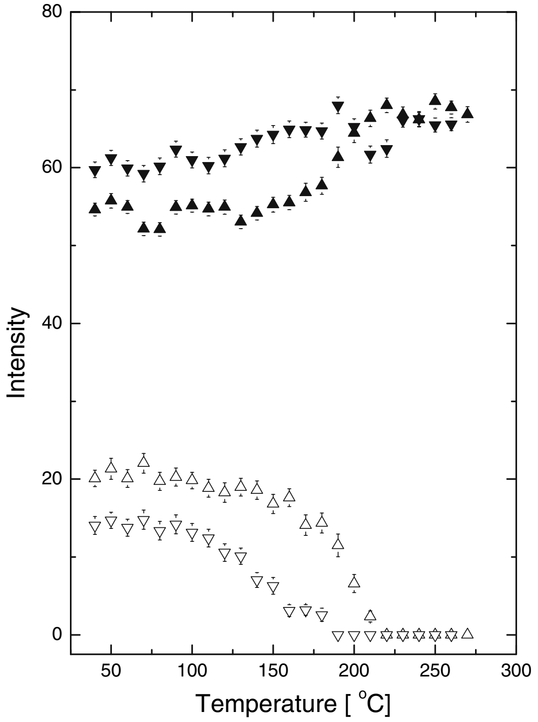

Fig. 2 The variation of the intensity of the (2 0 0) reflection (*solid symbol*) and the (0 0 2) reflection (*open symbol*) on heating (▲) and cooling (▼)

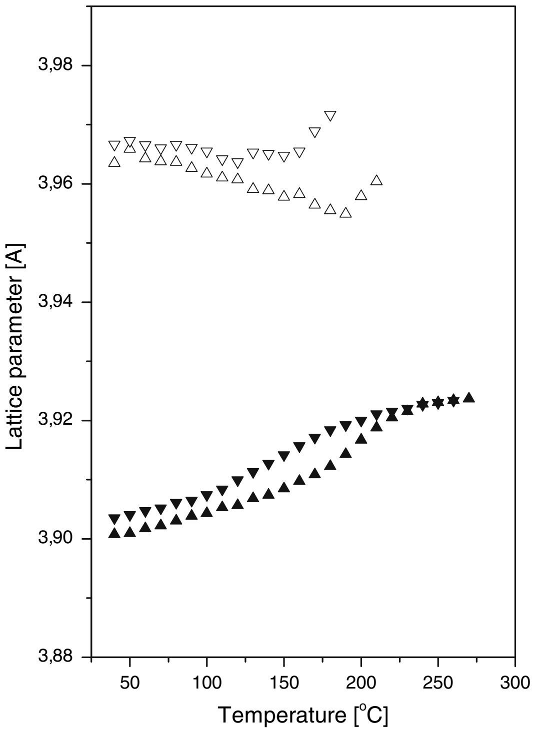

Fig. 3 The variation of the lattice parameter *a* (*solid symbol*) and *c* (*open symbol*) on heating (▲) and cooling (▼)

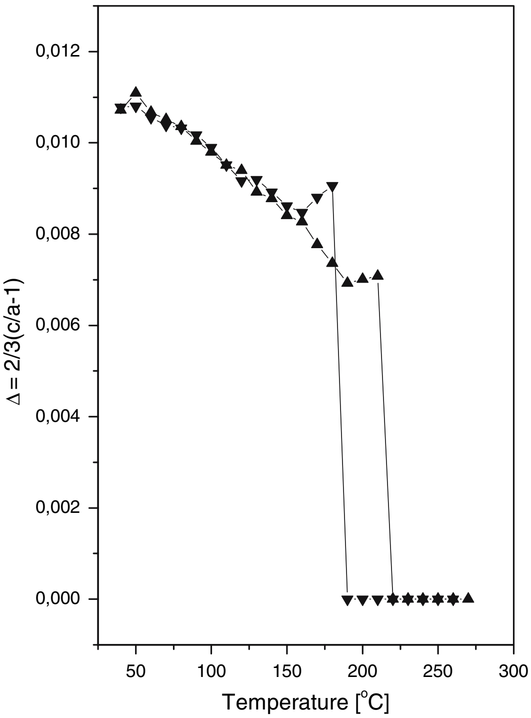

Fig. 4 The parameter Δ of the spontaneous strain at the tetragonal to cubic transformation on heating (▲) and cooling (▼)

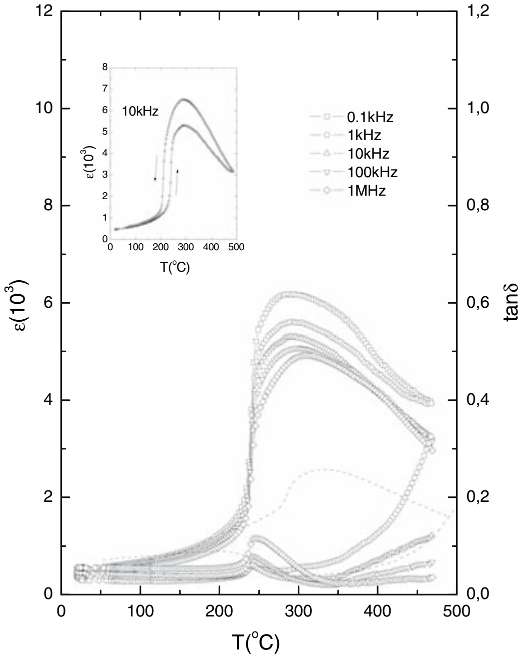

Fig. 5 Temperature/frequency dependence of weak field (E_{ac} = 0.01 kV/cm) electric permittivity and dielectric loss of NBTB12 ceramics (on heating). *Dashed lines* show, for comparison, the temperature dependence of the electric permittivity and dielectric loss of NBT ceramic at frequency 1 kHz. The insert shows the temperature dependence of electric permittivity on heating and cooling

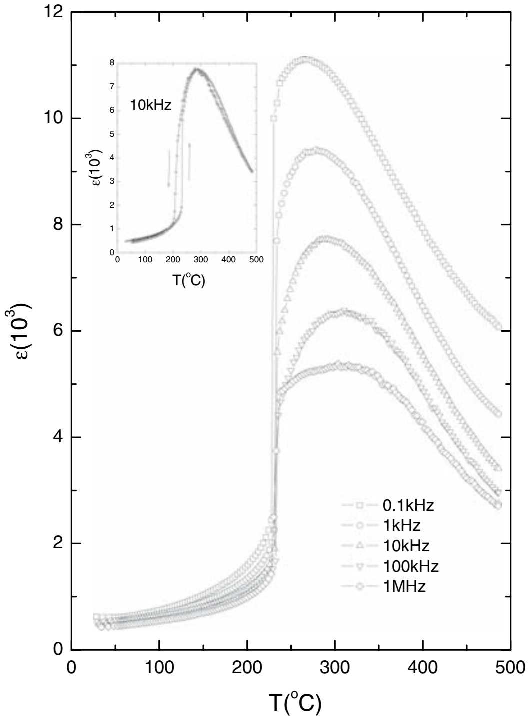

Fig. 6 Temperature/frequency dependence of electric permittivity of NBTB12 ceramics (on heating) at a.c. field intensity E_{ac} = 0.3 kV/cm. The insert shows the temperature dependence of electric permittivity on heating and cooling

TiO_3 [20] ceramics, where transformation from normal to relaxor ferroelectric phases were proposed. It can be suggested that the tetragonal-cubic transition should be divided into two parts [16, 20]. The first part with sharp increase of ε and tanδ is associated with structural changes; the second, the so called ''diffuse'' part is associated with the existence of cubic symmetry with small tetragonal (polar) regions, which lead to an increased relaxor-like behaviour. The local tetragonal regions have a random distribution of the tetragonal axes with respect to the 3 equivalent cubic symmetry [16, 20]. The pyroelectric and hysteresis loop measurements tend to support existence of polar regions in high temperatures in NBTB12 samples (see later).

After increase of the a.c. field intensity stronger frequency relaxation around T_m (Figs. 6, 7) can be observed. In addition, the thermal hysteresis is significantly reduced (insets in Figs. 5, 6). These results clearly demonstrate, that the relaxor behaviour can be enhanced by an a.c. field.

Figure 8 shows the temperature variation of the remanent polarization P_r obtained from pyroelectric measurements. It can be seen that Ba (12% mol) doping of NBT causes the decrease of the remanent polarization. The fastest changes of the P_r appear in the temperature range, where structural phase transition and rapid change of ε occur (Figs. 5, 6). It should be noted that the remanent polarization remains nonzero up to about 270 °C. Up to temperature ~235 °C the shape of the hysteresis loops is typical for a ferroelectric state in this material (not shown here). At temperatures above of about 235 °C these loops are deformed. Deformed hysteresis loops are typical for coexisting phases (polar and macroscopically non-polar phases [23, 27]). This, and fact that P_r falls to zero at about 270 °C, is the clue for the existence of polar regions in the temperatures above the structural phase transition.

Conclusions

NBTB12 ceramics were fabricated by ordinary sintering in air. Their crystal structure, determined by X-ray measurements, is tetragonal at room temperature and changes to cubic at about 220 °C. Dielectric, pyroelectric and hysteresis loops measurements revealed that normal-to-relaxor transformation takes place. Dielectric study has shown that relaxor-like dielectric characteristics was induced in NBT by doping of Ba. It was shown that this relaxor-like behaviour can be improved by increasing the a.c. field intensity. It is obvious that NBT-BT solid solutions are one of the promising lead-free materials for high frequency electromechanical transducer applications.

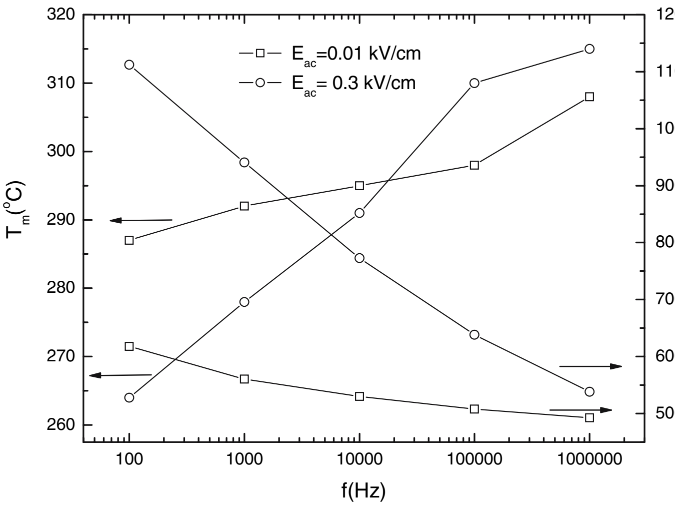

Fig. 7 Frequency dependence of T_m and ε_m of NBTB12 ceramics (on heating). The lines are guides for the eyes

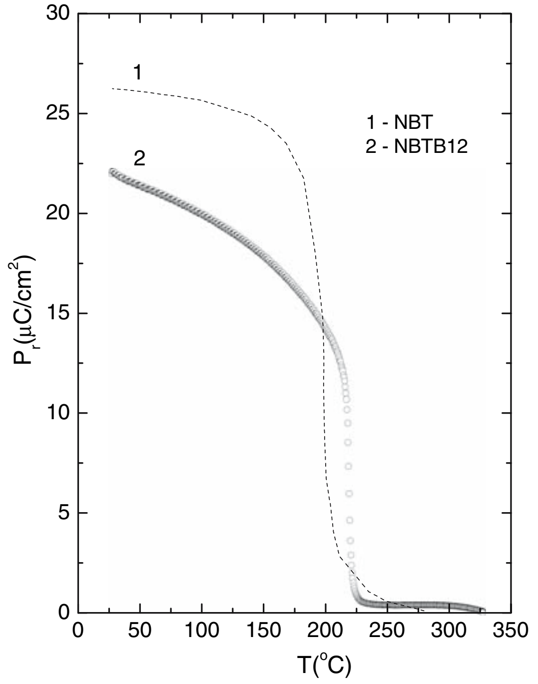

Fig. 8 Temperature dependence of the remanent polarization of NBTB12 ceramic. *Dashed line* shows for comparison temperature dependence of the remanent polarization for NBT ceramics

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