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Sodium-bismuth titanate based lead-free ferroelectric materials

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Abstract

In search of lead-free ferroelectric ceramics with improved properties, an investigation was carried out on barium and strontium-modified $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) ceramics. Many compositions among the Ba and Sr-modified ceramic materials exhibit diffuse phase transition and are characterised by a strong temperature and frequency dispersion of the permittivity which would be connected with the cation disorder in the A site of the perovskite unit cell.

Keywords: Dielectric properties; Lead-free titanates; Relaxation

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1. Introduction

Investigations of ferroelectric perovskite-type compounds with different distributions of the 6- or 12-fold coordination cations are more and more being increased as these materials are involved in the fabrication of many devices, e.g. capacitors, piezoelectric ultrasonic tranducers, electrostrictive actuators, SAW substrates, etc.[1–3] These materials have indeed high electromechanical characteristics which can be controlled either by doping or compositional change. The latter is connected in some cases with the onset of cationic disorder, the magnitude of which strongly influences the properties, mainly due to the dependence of the nature of the phase transition on the cationic distribution.

However, most of these materials are made from lead-bearing compounds, e.g. lead zirconate titanate (PZT), lead magnesium niobate (PMN), etc. So for environmental, health and social reasons, manufacturers are more and more constrained to reduce and ultimately eliminate the lead content of their materials. The search for alternative piezoelectric materials is now being focused on alkali niobates, modified bismuth titanates and systems in which a morphotropic phase boundary (MPB) will occur, that is bi or multiphasic systems in which one of the end phase is tetragonal and the other trigonal. Among them sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is trigonal at room temperature.[4–7] Solid solutions made from NBT and tetragonal titanates such as $PbTiO_3$ (PT), $BaTiO_3$ (BT) or $K_{0.5}Bi_{0.5}TiO_3$ (KBT) near their respective MPB would therefore be excellent candidates as low-lead or lead-free piezoelectric materials.[8–17]

Nevertheless, a necessary condition for successful production of high performing materials lies in the knowledge of their physical properties, especially the peculiarities accompanying the phase transitions in NBT and NBT-based systems which are not fully understood.

In this paper we will present experimental results and interpretation of structural and dielectric properties of some NBT-based materials belonging to the $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ (NBT–BT) and $Na_{0.5}Bi_{0.5}TiO_3$–$SrTiO_3$ (NBT–ST) systems.

2. Experimental

Solid solutions of the NBT–BT and NBT–ST systems were prepared by high temperature reaction of the corresponding reagent grade oxides or carbonates. After mixed in adequate stoichiometric proportions, they were calcined at 800 °C for 15 h and then crushed into powder using a ball mill for 15 min in acetone medium.

Disk-shaped ceramics with densities close to 95% of theoretical were obtained by conventional sintering the

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above prepared powders in air at 1050–1190 °C depending on the composition. After polishing, they were coated with a platinum paste fired at 800 °C and aged overnight at 100 °C. Low frequency dielectric measurements were carried out between room temperature and 800 °C (heating/cooling rate: 1 °C min^{-1}) at several frequencies from 100 Hz to 1 MHz using a HP 4194A impedance analyser.

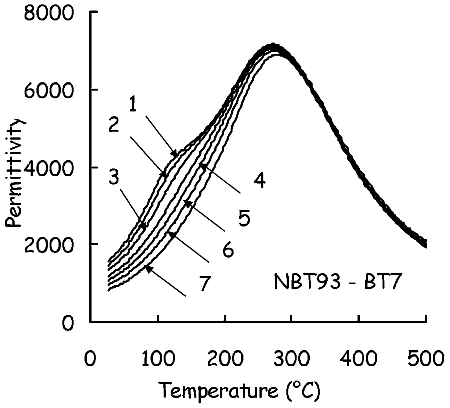

Fig. 1. Permittivity versus temperature for NBT93–BT7 (1: 10^2 Hz, 2: 10^3 Hz, 3: 10^4 Hz, 4: 10^5 Hz, 5: 2.5×10^5 Hz, 6: 5×10^5 Hz, 7: 10^6 Hz).

3. Results and discussion

3.1. NBT–BT system

Some recent studies of single crystals of the NBT–BT system have shown the interest of these materials for electromechanical actuation.[9,15,16] Most of the papers cited in literature have shown that the system presents a MPB around 7 mol% BT, all the materials across the full composition range being ferroelectric at room temperature. In the trigonal region, the dielectric behaviour of the NBT–BT solid solutions is, as expected, very

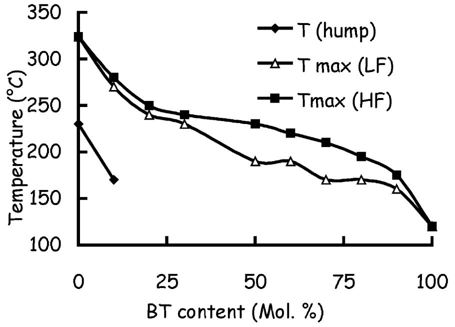

Fig. 3. Characteristic temperatures of the NBT–BT system.

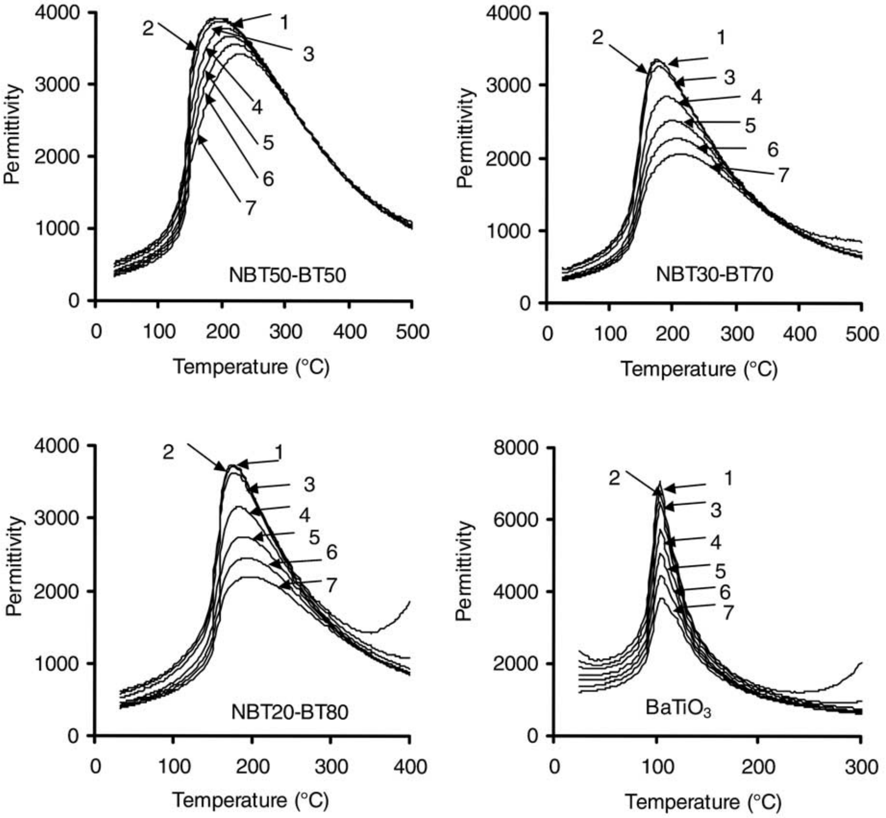

Fig. 2. Permittivity versus temperature for NBT50–BT50, NBT30–BT70, NBT20–BT80 and BT (1: 10^2 Hz, 2: 10^3 Hz, 3: 10^4 Hz, 4 : 10^5 Hz, 5: 2.5×10^5 Hz, 6: 5×10^5 Hz, 7: 10^6 Hz).

similar to the one observed for pure NBT or low-lead titanate and low-KBT materials as indicated in Fig. 1 which shows the variations of the permittivity of NBT–7 mol%BT ceramic material as a function of temperature and frequency.[17]

A careful examination of the figure reveals that both the temperatures of the maximum permittivity (T_m) and of the hump (T_1) have been shifted towards the low temperature side. This behaviour is not significantly changed when the compositions crossed the limit of the MPB. Nevertheless, the behaviour of the permittivity is strongly modified when the barium content increases. Fig. 2 presents the results obtained for some Ba-rich compositions from 50 to 100 mol% Ba ($BaTiO_3$). Increasing Ba content influences both the temperature at which the tetragonal–cubic phase transition occurs and the shape of the permittivity curves. Taking the temperature of maximum low frequency permittivity as the Curie temperature and as expected for classical ferroelectric solid solutions, Fig. 2 shows that T_C decreases monotonously from ca. 200 °C for $NBT_{50}BT_{50}$ down to 120 °C for $BaTiO_3$. In addition, excepted for pure $BaTiO_3$, the evolution of the permittivity shows a strong frequency dependent dispersion.

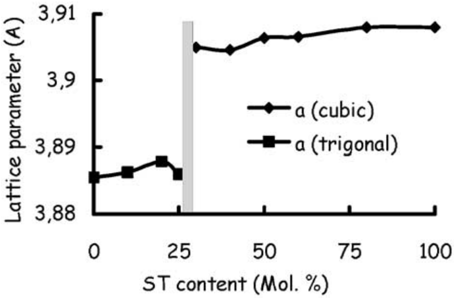

Fig. 4. NBT–ST system: lattice parameters versus composition.

The maximum of the permittivity decreases as the measurement frequency increases and its temperature is shifted towards high temperatures as well. However, this behaviour is more pronounced for NBT-rich materials

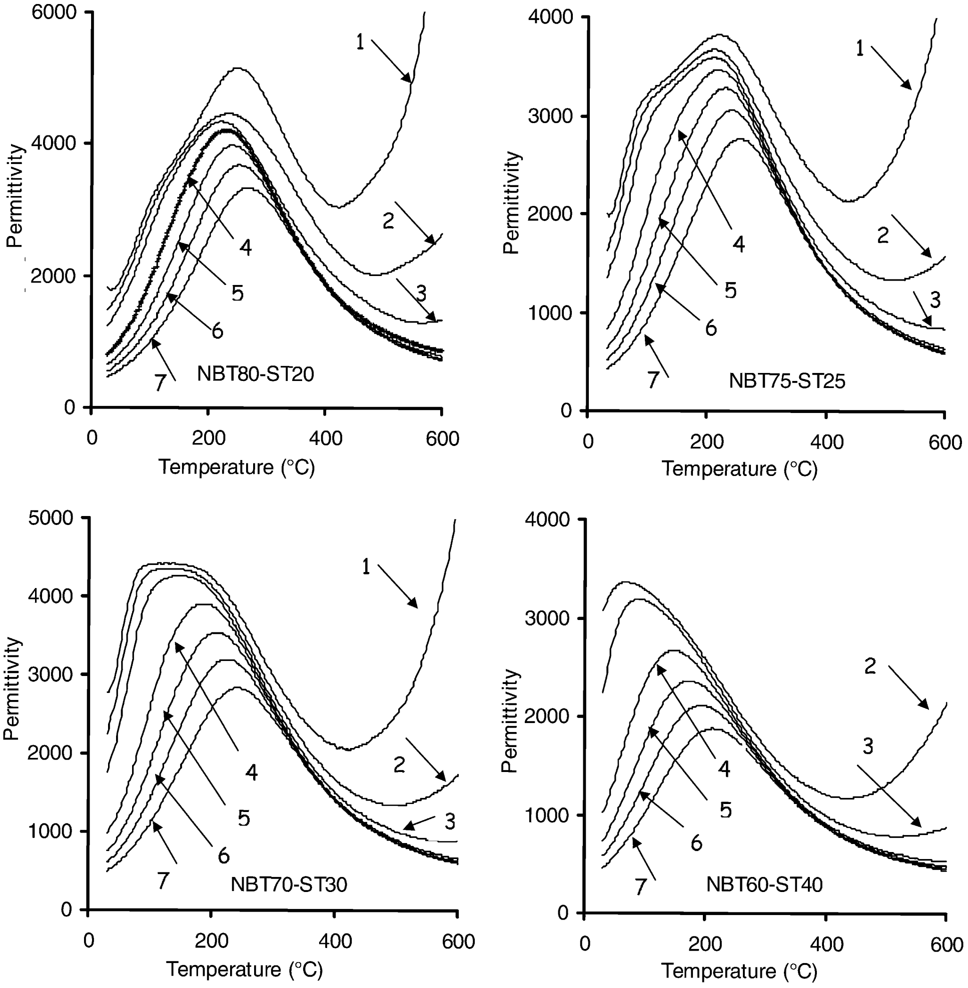

Fig. 5. Permittivity versus temperature for NBT-rich NBT–ST materials (1: 10^2 Hz, 2: 10^3 Hz, 3: 10^4 Hz, 4: 10^5 Hz, 5: 2.5×10^5 Hz, 6: 5×10^5Hz, 7: 10^6 Hz).

than for the BT-rich ones. As expected, a NBT-like behaviour (hump at 170–230 °C, T_m at 280–320 °C) is observed in the trigonal region.

The overall dielectric behaviour of the NBT-BT materials can be summarised as shown in Fig. 3. When increasing the Ba content, a relaxor-like behaviour occurs, the maximum amplitude of which ($T_{m[\text{high frequency}]} - T_{m[\text{low frequency}]}$) being located in the midrange of compositions (50–70 mol% BT).

3.2. NBT–ST system

In contrast with NBT–BT, there would be no MPB in NBT–ST because ST does not present any phase transition from the room temperature cubic symmetry. In addition, ST is non ferroelectric so that the behaviour of NBT–ST materials would act as a basis for comparison, especially concerning the domain observed between 200 and 320 °C for NBT, the temperature range of which would be expected to change with the composition. When ST is substituted into NBT, the room temperature crystal symmetry remains trigonal up to 26–27 mol% ST. For compositions richer than 30 mol% ST, the materials adopt the cubic symmetry of ST (Fig. 4). These results are in agreement with partial investigations previously published.[8,14]

The variations of the permittivity versus temperature and frequency present the following main features as the ST content increases (Figs. 5 and 6):

(i) For compositions with trigonal symmetry both temperatures T_m and T_l are shifted to the low temperature hand side, their difference decreases but the dispersion of the permittivity around T_m still remains.
(ii) For compositions with cubic symmetry, T_m and T_l have merged and the temperature of the unique maximum strongly decreases.
(iii) In the whole composition range, a strong dispersion of the permittivity occurs.

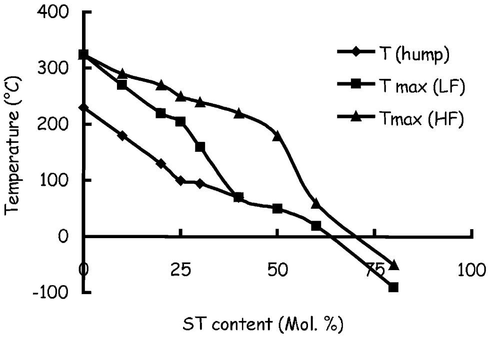

Fig. 7. Characteristic temperatures of the NBT–ST system.

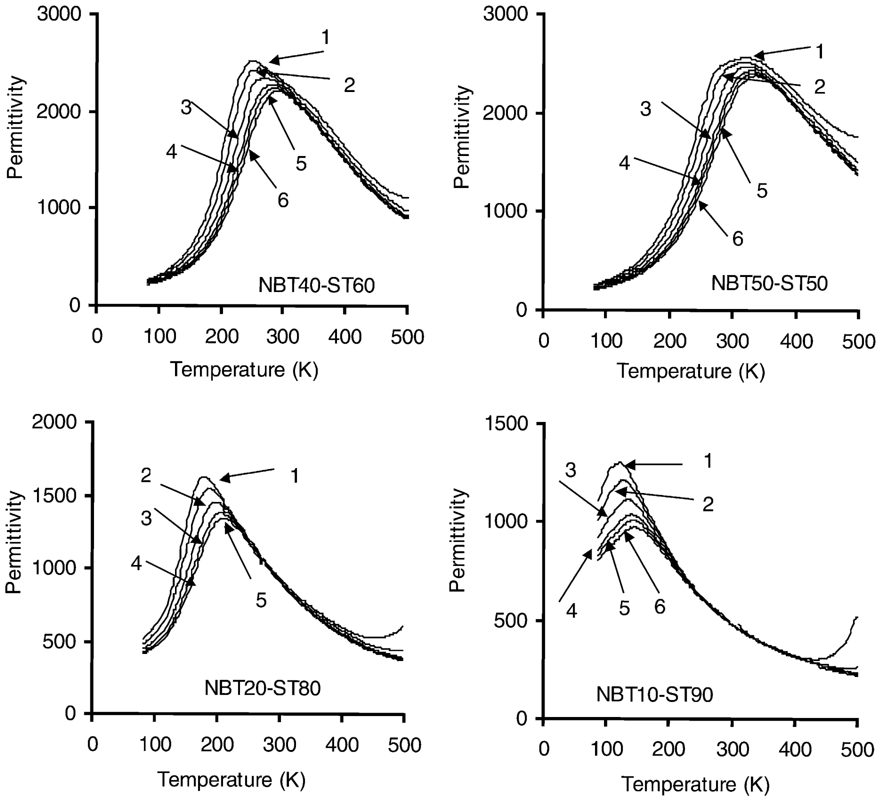

Fig. 6. Permittivity versus temperature for ST-rich NBT–ST materials (1: 10^2 Hz, 2: 10^3 Hz, 3: 10^4 Hz, 4: 10^5 Hz, 5: 2.5×10^5 Hz, 6: 5×10^5 Hz, 7: 10^6 Hz).

The results reveal that the maximum of the permittivity at low frequency for compositions richer than 60 mol% ST would occur below room temperature as illustrated for compositions close to ST in Fig. 6.

The evolution of the permittivity for the trigonal compositions are consistent with a narrowing of the antiferroelectric intermediate phase which seems to vanish around 40 mol% ST as shown in Fig. 7. For ST-richer compositions, the maximum of the permittivity decreases and is shifted to higher temperature as the measuring frequency increases. This behaviour is similar to conventional relaxor ferroelectrics. For temperatures higher than T_m, the permittivity varies in a way observed for NBT–BT materials with similar compositions.

Previously published data about Bi-modified $SrTiO_3$ have shown that increasing Bi concentration leads to the occurrence of a ferroelectric relaxor state connected with the probable existence of polar regions in a non polar matrix.[18] The results presented here for ST-rich compositions could be interpreted similarly. In addition, such a behaviour is observed in preliminary experiments now in progress within the parent system NBT–$CaTiO_3$. In any case the origin of such a behaviour might be in close connection with the ordered or disordered occupation of the 12-fold coordinated A site of the perovskite cell. Further investigations are necessary to deepen the dielectric properties of these materials, especially concerning their behaviour at low temperature in the light of the usual theories of relaxation and in connection with accurate determination of the actual crystal structure.

4. Conclusion

From dielectric measurements in wide temperature ($-170/+600$ °C) and frequency (10^2–10^6 Hz), it was established that the properties of $Na_{0.5}Bi_{0.5}TiO_3$ ceramics are strongly modified by $BaTiO_3$ or $SrTiO_3$ substitutions. In both cases a relaxor-like behaviour occurs at temperatures depending on the composition. For BT-modified materials, this character decreases as the BT content increases. For ST-modified materials, the intermediate antiferroelectric phase vanished at about 40 mol% ST and the relaxor-like behaviour is maintained in the whole composition range.

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