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Relaxor behaviour of low lead and lead free ferroelectric ceramics of the $Na_{0.5}Bi_{0.5}TiO_3$–$PbTiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ systems

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Abstract

Ceramics with compositions belonging to the $Na_{0.5}Bi_{0.5}TiO_3$–$PbTiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ systems were fabricated by natural sintering of powders prepared by thermal decomposition of adequate precursor solutions. The ferroelectric to paraelectric phase transitions were studied by variable temperature X-ray diffractometry, differential scanning calorimetry and impedance measurement in a wide range of temperature and frequency. In contrast with pure NBT, both the permittivity and dielectric loss of the NBT-rich solid solutions show a strongly temperature and frequency dependent behaviour. The permittivity decreases and its maximum is shifted towards high temperatures as the frequency increases. In the high temperature range, the thermal variation of the permittivity is well described by a law $\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=C(T-T_m)^{\gamma}$ with γ close to 1.5. Such a relaxor-like behaviour is interpreted in terms of cation disorder due to the statistical repartition of (Na,Bi) and Pb (or Na and K). This would be one very rare case of relaxor phenomena correlated with the A-site occupancy in perovskite-like materials. © 2001 Published by Elsevier Science Ltd.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Relaxation

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1. Introduction

Sodium-bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$, hereafter NBT) has a rhombohedral perovskite-like structure ($a=0.389$ nm, $\alpha=89.6°$).[1] The Na^+ and Bi^{3+} ions are randomly distributed at the 12-fold cubooctahedral sites. NBT is ferroelectric at room temperature and undergoes a series of temperature induced phase transitions: (i) at ~230°C the permittivity shows a flat, frequency dependent hump assigned to ferroelectric (rhombohedral)–antiferroelectric (tetragonal) phase transition, (ii) at ~520°C, the symmetry changes to cubic.[2] In addition, at ~320°C, the permittivity has a diffuse maximum the temperature of which being frequency independent.[3–5] Appropriate cation modifications (e.g. Pb^{2+}, K^+, alkali-earth AE^{2+}) are likely to influence both the temperature of phase transitions and the dielectric behaviour. It has been already shown that, in the NBT–PT system, the solid solution keeps the rhombohedral symmetry up to 12–18 mol% PT.[6,7] The purpose of this paper is to study the changes of the permittivity behaviour and their connection with phase transitions when lead or potassium are substituted for (Na,Bi) in $Na_{0.5}Bi_{0.5}TiO_3$.

2. Experimental

Solid solutions of the NBT–PT and NBT–KBT systems were prepared by a sol-gel route. The precursor solutions were prepared by mixing bismuth and sodium and/or lead and potassium acetates in acetic acid and poured in a solution of titanium isopropoxide in isopropanol. The mixtures were continuously stirred for 2 h at 100°C. After cooling down to room temperature homogeneous sols were obtained which can be stored unchanged for several hours. After drying for 10 h

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at 350°C, the precursors were calcined for 1–50 h at 700–900°C depending on the composition. The crystallisation process and the phase analyses were performed using a Siemens D5000 powder diffractometer fitted with an Anton Parr HTK variable temperature attachment.

Disk-shaped ceramics with densities close to 95% of theoretical were obtained by conventional sintering in air at 1050–1190°C. After polishing, they were coated with a platinum paste fired at 650°C and aged overnight at 100°C. Low frequency dielectric measurements were carried out between room temperature and 800°C at several frequencies from 100 Hz to 1 MHz using a HP 4194A impedance analyser.

3. Results and discussion

3.1. NBT-rich system, rhombohedral symmetry

As mentioned before, NBT is rhombohedral and ferroelectric at room temperature. Fig. 1 shows the variations of the permittivity of a sintered sample of NBT as a function of temperature in the frequency range 100 Hz–1 MHz. According to previous data, a frequency dependent behaviour is observed (i) as a hump between room temperature and ~ 200°C (T_1) and (ii) as a dispersion of the permittivity for temperatures higher than ~ 320°C (T_m). The marked increase of the permittivity at high temperature and low frequencies is significant of space charge polarisation and associated ionic conductivity. On cooling, these characteristic temperatures are shifted by 15–20°C downwards.

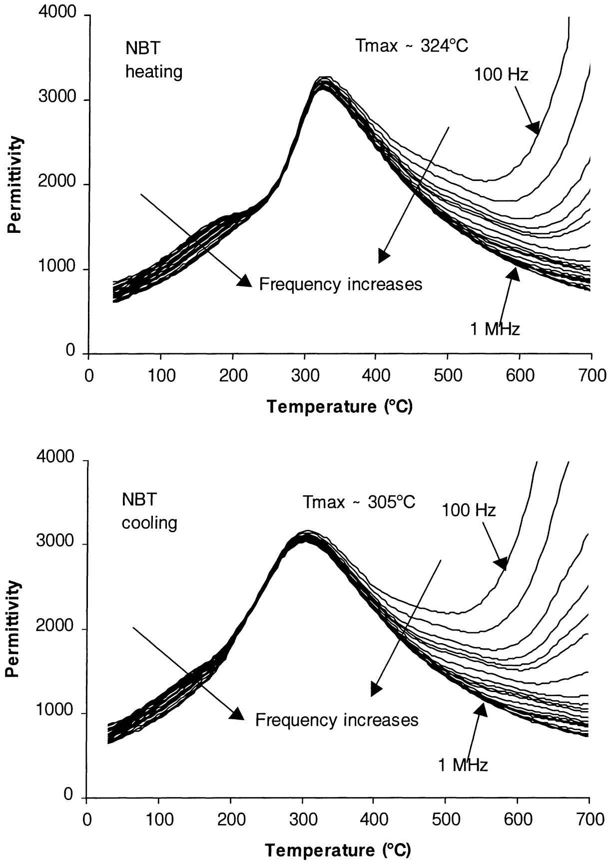

Fig. 1. Temperature dependence of the permittivity of NBT at heating and cooling for several frequencies.

As already shown by several authors, the $(Na_{0.5}Bi_{0.5})_{1-x}Pb_xTiO_3$ (NBT-PT) system is characterised by a morphotropic phase boundary located in the composition range $0.13 < x < 0.18$ separating the rhombohedral sodium/bismuth rich compounds from the tetragonal lead rich ones.[5–7] In the rhombohedral symmetry range, the values of T_m obtained from low frequency measurements (1 kHz–1 MHz) show a minimum for $x \sim 0.06$–0.08 (Fig. 2), confirmed by XRD and DSC analyses. In contrast with unmodified NBT, the thermal evolution of the permittivity is strongly frequency dependent.

As shown in Fig. 3 for the composition NBT97PT3 ($x = 0.03$), the hump at T_1 is softened and even disappeared whereas T_m increases as the measurement frequency increases in a way similar to that observed for relaxor materials. Even after repeated experiments at heating and cooling, this behaviour remains almost unchanged. As Na^+ and Bi^{3+} are randomly distributed in the 12-fold coordination site, the relaxation-like behaviour would reasonably attributed to some disorder induced by the presence of Pb^{2+} as well as some lead vacancies due to the sintering process.

For temperatures higher than T_m, the variation of the permittivity does not follow the classical Curie–Weiss law. Whatever the measurement frequency, the permittivity varies according to the law $\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = C(T - T_m)^{\gamma}$ with close to 1.5 as clearly shown in Fig. 4 for 10^5 Hz. In this relation γ acts as a diffusion coefficient and ranges

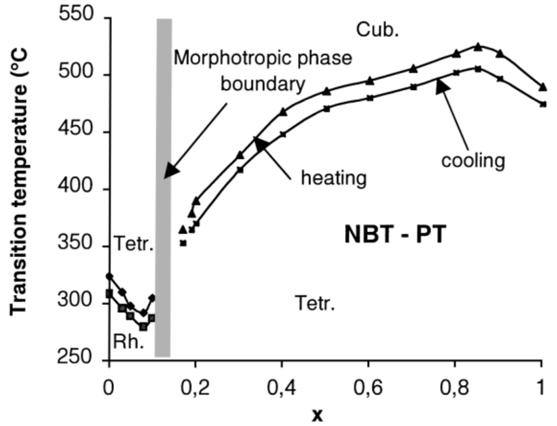

Fig. 2. Transition temperatures vs composition for the NBT–PT system.

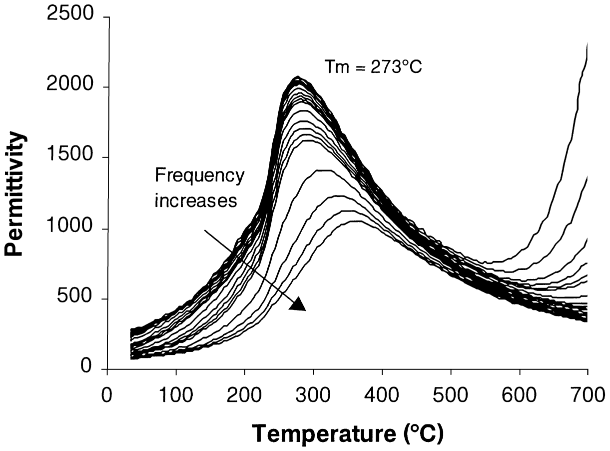

Fig. 3. Temperature dependence of the permittivity of NBT97PT3 at cooling for several frequencies.

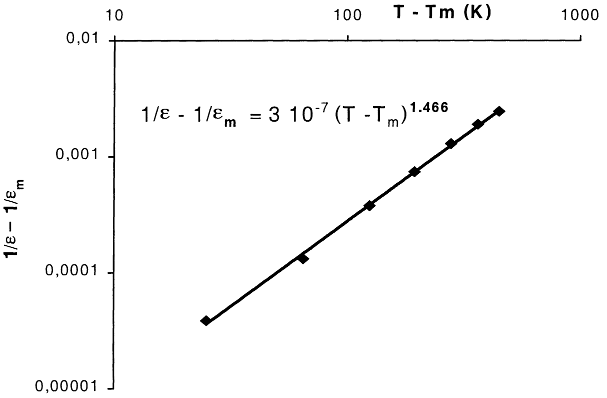

Fig. 4. Reciprocal permittivity of NBT97PT3 vs T–T_m.

between 1 and 2 for materials with a diffuse phase transition.[8] This behaviour would be significant of a relaxation process due to cation mixture.

For the $Na_{0.5-x}K_xBi_{0.5}TiO_3$ (NBT–KBT) system, the morphotropic phase boundary seems to be located in the composition range $0.4 < x < 0.5$.[7] In the rhombohedral symmetry range, the variations of the permittivity are similar to those observed for NBT–PT, but show a more diffuse character (Fig. 5).

3.2. PT-rich system, tetragonal symmetry

For compositions above the upper limit of the MPB, the behaviour of the permittivity is strongly dependent on the lead content. Close to the MPB, the variations of the permittivity are significant of a diffuse phase transition with some frequency dispersion. As the lead rate increases, the transition becomes sharper as it does for pure lead titanate.

In order to know more about the origin of the diffuse character of the phase transition and the occurrence of a relaxation process, dielectric measurements were conducted after several firing procedures of samples with composition close to the MPB, e.g. NBT82PT18.

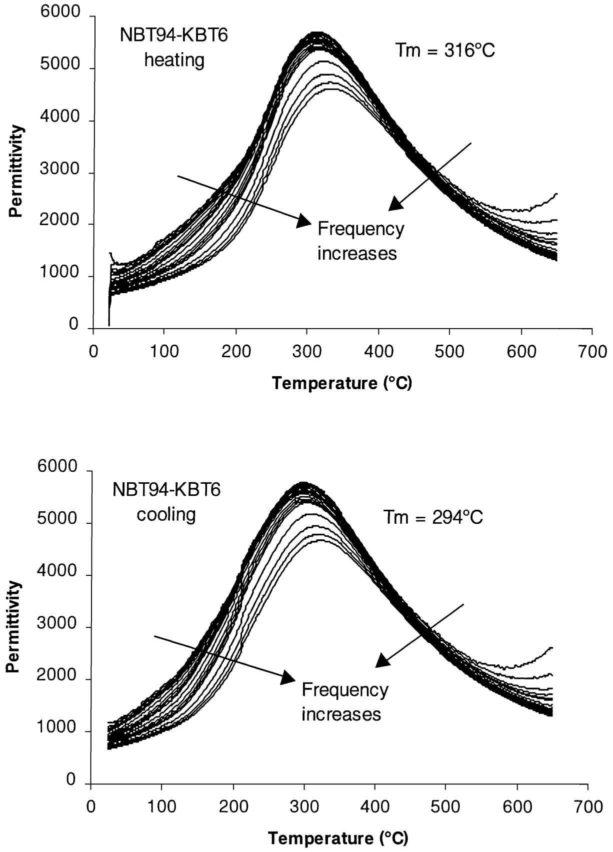

Fig. 5. Temperature dependence of the permittivity of NBT94–KBT6 at heating and cooling for several frequencies.

Fig. 6a shows the thermal variations of the permittivity of a sample fired at 1190°C. At low frequencies (< 20 kHz) two maximums were observed: the first one occurs at about 345°C, the second one appears between 500 and 600°C and is frequency dependent. At higher frequencies, the temperature of the first maximum increases with temperature and its intensity decreases as well, whereas the second maximum vanishes. The same sample was then fired again at 1190°C in PbO atmosphere. The results are shown in Fig. 6b. The high temperature maximum has disappeared and there remains only a little increase of the temperature of the first maximum for the highest frequencies. In lead titanate the occurrence of a relaxation-like behaviour of the permittivity at high temperature was assigned to conductivity connected with both grain boundary and oxygen vacancies.

Sintering in PbO atmosphere is therefore likely to suppress such phenomenon by lowering the number of oxygen vacancies and by improving the grain boundaries. In addition the decrease of the temperature range of the first maximum would be related to the

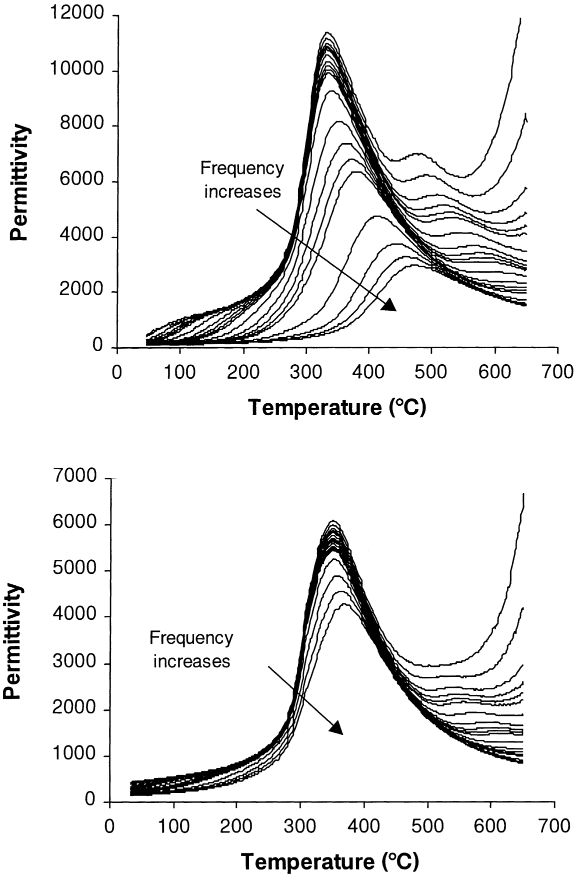

Fig. 6. Thermal dependence of the permittivity of NBT82PT18 at cooling for several frequencies: (a) firing at 1190°C in air; (b) firing at 1190°C in PbO atmosphere.

diminution of lead vacancies, which limits the cation disorder without full suppression of the relaxation process.

4. Conclusion

The dielectric properties of low lead (NBT–PT) and lead free ferroelectric (NBT–KBT) ceramics prepared from sol-gel derived powders have been studied as a function of temperature and frequency. A relaxor-like behaviour was observed for NBT-rich materials and attributed to cation disorder in the 12-fold coordination sites. Sintering in PbO atmosphere would soften this phenomenon.

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