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Journal of the European Ceramic Society 27 (2007) 2481–2484

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Dielectric properties of new perovskite ceramics $(Na_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ and $(K_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$

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Received 14 June 2006; received in revised form 24 August 2006; accepted 2 September 2006
Available online 30 October 2006

Abstract

New perovskite ceramics $(Na_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ (NBMT) and $(K_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ (KBMT) were synthesized using solid-state reaction method. These two new ceramics have cubic symmetry structure at room temperature. Both NBMT and KBMT show a frequency-dependent broad dielectric maximum ε'_m around 200–330 °C, and the dielectric constant ε' varies from several hundreds at 20 °C to about two thousands of ε'_m. No ferroelectric behaviour is observed. Between 10^2 and 10^6 Hz, the ε' exhibits frequency dispersion in rather wide temperature range. The frequency dependence of ε' follows the formula, $\varepsilon'(\nu) = \varepsilon'(1\,\text{Hz}) - B \log \nu$, at low temperature side of the T_m.

Keywords: Perovskites; Dielectric properties; Powders-solid state reaction; (Na, Bi)(Mg, Ti)O_3

1. Introduction

$(Na_{1/2}Bi_{1/2})TiO_3$ (NBT) and $(K_{1/2}Bi_{1/2})TiO_3$ (KBT) are complex perovskite materials. They are ferroelectrics at room temperature. NBT exhibits two structural phase transformation from ferroelectric rhombohedral phase to tetragonal (200–350 °C) and to paraelectric cubic phase (520–540 °C). KBT undergoes only a single-phase transformation below 250 °C, between ferroelectric tetragonal phase and paraelectric cubic phase. NBT and KBT ceramics show a broad maximum of dielectric constant at ∼320 and ∼380 °C, respectively. But the maxima do not correspond to any phase transition.[1–6] Several solid solutions of NBT–KBT and NBT with $BaTiO_3$ (BT), $PbTiO_3$, $SrTiO_3$, and $PbZrO_3$ have been studied. Among them, NBT–KBT and NBT–BT systems present attractive high piezoelectric properties.[7–13]

In this work, two new perovskite materials $(Na_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ (NBMT) and $(K_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ (KBMT) are synthesized using routine electro-ceramic process. Compared with compositions of NBT and KBT, the contents of Bi^{3+} ions at the A lattice site in NBMT and KBMT increase 25 at%, and simultaneously, 25 at% contents of Ti^{4+} ions at the B lattice site are substituted by Mg^{2+} ions, which are not ferroelectrically active.

2. Sample preparation

Stoichiometric amount of reagents Bi_2O_3, TiO_2, $MgCO_3$, and Na_2CO_3 or K_2CO_3 powders were wet mixed by ball milling, and then presintered for 2–5 h at temperatures ranging from 750 to 900 °C in a closed corundum crucible. The presintered powder was ball milled and dried. Pellets 12 mm in diameter and 1–2 mm thick were pressed using 10% PVA binder. Samples were fired at temperatures ranging from 1000 to 1100 °C for 1 h.

Crystal structures of the samples were detected using a Rigaku D/max 2400 X-ray diffractometer (XRD) with Cu Kα radiation. The microstructures were observed using a Hitachi S-2700 scanning electron microscope (SEM). The dielectric constant ε' and dielectric absorption ε'' were measured on an automated system, wherein a temperature control sample chamber and an Agilent 4284A inductance–capacitance–resistance (LCR) meter, which can cover a frequency range from 20 Hz to 1 MHz, were controlled by a personal computer. Two temperature chambers were used for different temperature range measurement from −150 to 170 °C, and from room temperature to 650 °C, respectively. Current–field relation was measured on an automatic ferroelectric test system of aixACT TF-ANALY2ER2000. The measurements were carried out with

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doi:10.1016/j.jeurceramsoc.2006.09.003

electric field strength up to 60 kV/cm. Applied electric field signal is triangular, and a period time is 1 s.

3. Results and discussion

Fig. 1 shows the XRD patterns for ceramics NBMT and KBMT. All peaks could be indexed based on the perovskite structure and no second phase was observed within the detection limit of XRD. Using a $Pb(Mg_{1/3}Nb_{2/3})O_3$-type cubic (Pm3m) model,[14] preliminary unit cell parameter a is 0.393 nm for NBMT, and 0.398 nm for KBMT, respectively. The microstructures of ceramics NBMT and KBMT are shown in Fig. 2. The grain size is in the range of 2–5 μm.

The loops of current density versus electric field for ceramics NBMT and KBMT at room temperature are presented in Fig. 3. Applied electric field maximum reached 60 kV/cm for NBMT and 40 kV/cm for KBMT, respectively. The current density did not exhibit charge/discharge peaks, which indicate ferroelectricity. According to the crystal structure symmetry and the electric polarization property, NBMT and KBMT ceramics might not have ferroelectric properties around and above room temperature. The leakage conductivities were estimated by the relationship of the current and field, which is $\sim 7 \times 10^{-8}$ S/m for NBMN and $\sim 4 \times 10^{-7}$ S/m for KBMN, respectively.

High-temperature variation of dielectric constant ε' and dielectric absorption ε'' at different frequencies for two compositions are shown in Fig. 4. NBMT and KBMT exhibit very similar dielectric behaviour. Their dielectric properties present strong relaxation behaviour. The temperature T_m of dielectric constant maximum ε'_m is 218 °C at 100 Hz, 235 °C at 1 kHz, 259 °C at 10 kHz, 288 °C at 100 kHz, and 322 °C at 1 MHz, respectively, for NBMT sample, and 255 °C at 10 kHz, 283 °C at 100 kHz, and 323 °C at 1 MHz, respectively, for KBMT sample. ΔT_m $(=T_{m,1\,MHz} - T_{m,100\,Hz})$ is 104 °C for NBMT, which is much wider than those of normal relaxor ferroelectric ceramics. The ε' decreases very smoothly with increasing temperature on the high-temperature side of T_m. For instance, the temperature of $0.99\varepsilon'_m$ of NBMT at 100 kHz is 330 °C, which is 42 °C higher than T_m of 288 °C. Like normal relaxor ferroelectrics, however, the rising section of dielectric absorption ε'' peak has much weaker frequency dependence compared with the falling section, and the peak measured at lower frequency is covered by this one measured at higher frequency.

There are strong frequency dispersion in $\varepsilon'(T)$ on the low-temperature side of T_m (Figs. 4 and 5). The dielectric frequency dispersion becomes week gradually with decreasing temperature. The frequency ν dependence of ε' and ε'' for NBMT between 0.1 and 1000 kHz at different temperatures is plotted in

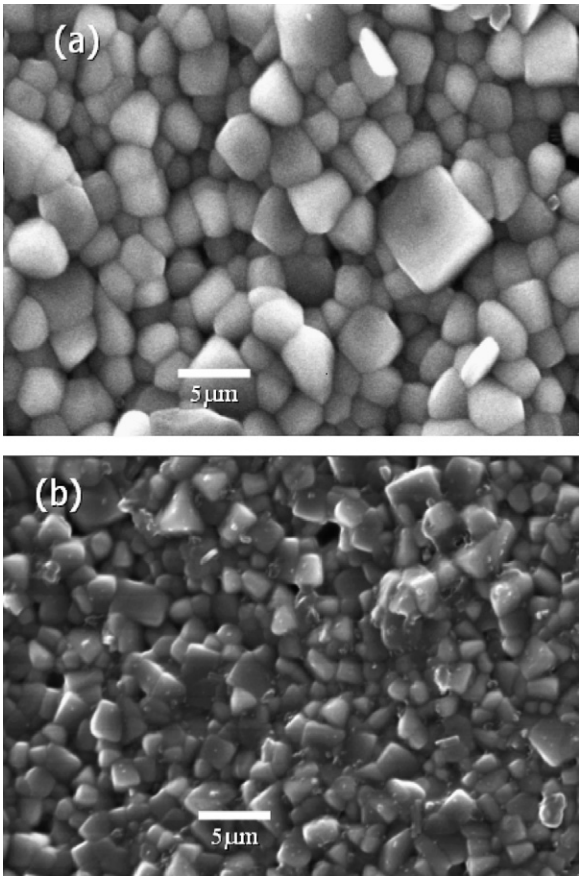

Fig. 2. SEM micrographs of (a) NBMT sintered at 1050 °C and (b) KBMT sintered at 1070 °C.

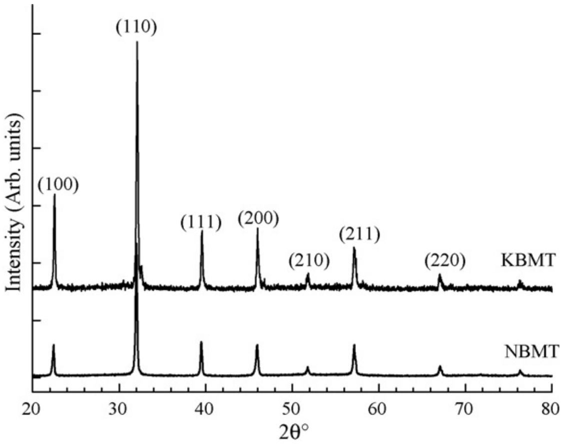

Fig. 1. X-ray diffraction patterns at room temperature for ceramics NBMT and KBMT.

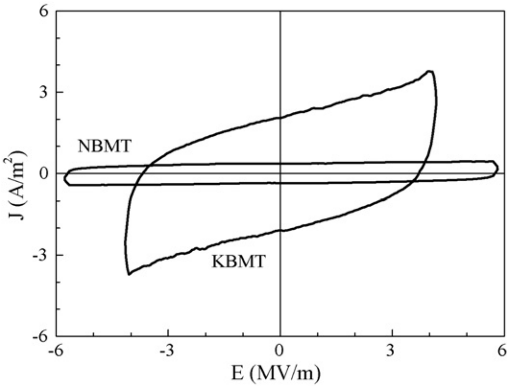

Fig. 3. Current intensity–field loop at room temperature for ceramics NBMT and KBMT.

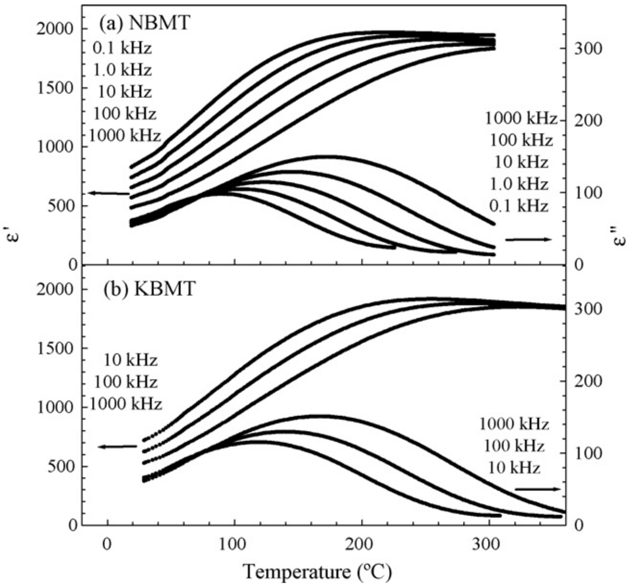

Fig. 4. Temperature dependence of dielectric constant ε' and dielectric absorption ε'' at different frequencies for ceramics NBMT (a) and KBMT (b).

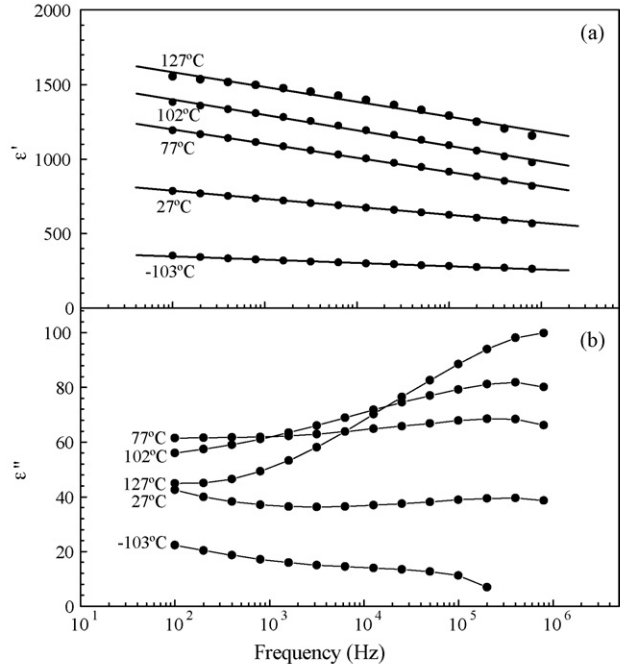

Fig. 6. ε' (a) and ε'' (b) vs. frequency at different temperature for ceramic NBMT.

Fig. 6. Below 102 °C, ε' very well obeys the following formula,

$$\varepsilon'(\nu) = \varepsilon'(1\,\mathrm{Hz}) - B \log \nu, \qquad (1)$$

where $\varepsilon'(1\,\mathrm{Hz})$ is extrapolated dielectric constant ε' at 1 Hz, and constant B indicates the intensity of the dielectric dispersion, which increases with temperature till 110 °C. The values of constant $\varepsilon'(1\,\mathrm{Hz})$ and B at different temperatures are listed in Table 1. Dielectric absorption ε'', representing energy dissipation, varies little during 10^2 and 10^6 Hz and increases with temperature till 90 °C, see Figs. 4, 5(b), and 6(b). Above ∼100 °C, $\varepsilon''(T)$ starts its different variation at different frequencies. Contrary to $\varepsilon'(T)$, $\varepsilon''(T)$ at higher frequency has higher maximum than that of $\varepsilon''(T)$ at lower frequency. KBMT ceramics present the analogous dispersion behaviour.

Since both the magnitude of ε' and the degree of dielectric frequency dispersion increase with temperature below T_m, $\Delta\varepsilon'/\varepsilon'\,(=(\varepsilon'_{\nu_\mathrm{m}} - \varepsilon'_{\nu_\mathrm{n}})/\varepsilon'_{\nu_\mathrm{m}})$ is employed to represent relative dielectric frequency dispersion (Fig. 7). The ratio of frequency $\nu_\mathrm{n}/\nu_\mathrm{m}$ (=400 kHz/25.3 kHz, 25.3 kHz/1.6 kHz, and 1.6 kHz/0.1 kHz) is almost the same for the selected three frequency intervals. The difference of $\Delta\varepsilon'/\varepsilon'$ in different frequency intervals is lower than 10% for any fixed temperature during measuring temperature range. There is still a round maximum in the plot of $\Delta\varepsilon'/\varepsilon'$ versus temperature, and the temperature T'_m of maximal $(\Delta\varepsilon'/\varepsilon')_\mathrm{m}$ shifts towards high temperature with increasing frequency. The T'_m of NBMT is between 60 and 90 °C, which is evidently much lower than the T_m. Above the T'_m, the relative dielectric frequency dispersion decreases quickly. Although the absolute dielectric frequency dispersion becomes apparently strong in the temperature range near T_m, the relative dielectric frequency dispersion is the same as, or even less than that in the low temperature range.

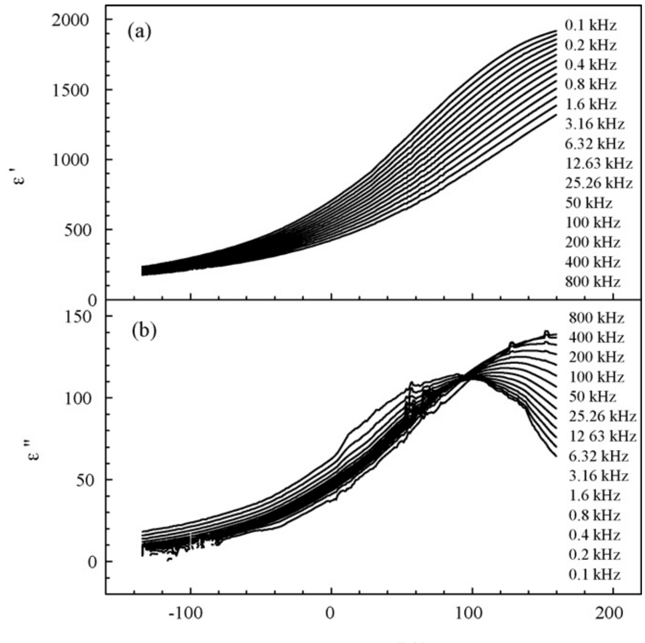

Fig. 5. Variation of ε' (a) and ε'' (b) with temperature from −130 to 160 °C at different frequencies for ceramic NBMT.

Table 1
Constants of formula $\varepsilon'(\nu) = \varepsilon'(1\,\mathrm{Hz})_\mathrm{z} - B \log \nu$ for NBMT ceramic at different temperatures

T (°C)	$\varepsilon'(1\,\mathrm{Hz})$	B
−103	391	21.9
23	897	54.9
77	1389	95.1
102	1607	103.6
127	1783	99.8

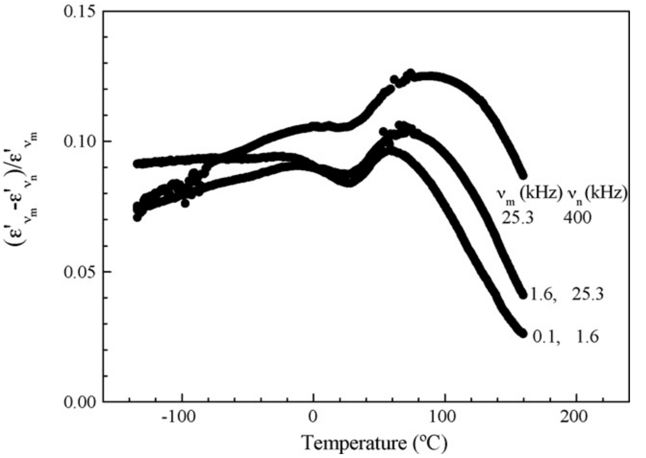

Fig. 7. Temperature dependence of relative dielectric frequency dispersion $(\varepsilon'_{\nu_m}-\varepsilon'_{\nu_n})/\varepsilon'_{\nu_m}$ for ceramic NBMT.

The dielectric relaxation behaviour of NBMT and KBMT is analogous to that of relaxor ferroelectrics on the whole, though there are some distinctions mentioned above. $(Na_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ and $(K_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ can be expressed as $0.5(Na_{1/2}Bi_{1/2})TiO_3$-$0.5Bi(Mg_{1/2}Ti_{1/2})O_3$ and $0.5(K_{1/2}Bi_{1/2})TiO_3$–$0.5Bi(Mg_{1/2}Ti_{1/2})O_3$, respectively. $(Na_{1/2}Bi_{1/2})TiO_3$ (NBT) and $(K_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ (KBT) are ferroelectrics below 230 °C. $Bi(Mg_{1/2}Ti_{1/2})O_3$ is a paraelectric material with cubic symmetry.[15] As much as 50 mol% paraelectric additives in NBMT and KBMT dilutes the polar nano-regions related to the components of NBT or KBT, so that the polar nano-regions could not induce their neighbours to become macro-domains as temperature decreases from T_m to room temperature. Accordingly, ceramics NBMT and KBMT do not exhibit ferroelectric properties at room temperature which is far below their T_m, and their dielectric relaxation behaviour might still originate from the polar nano-regions.

4. Conclusions

New perovskite materials $(Na_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ and $(K_{1/4}Bi_{3/4})(Mg_{1/4}Ti_{3/4})O_3$ were fabricated by solid-state reaction method. Their crystal structures at room temperature are cubic symmetry. No ferroelectricity has been detected in NBMT and KBMT ceramics. However, a frequency-dependent broad maximum of dielectric constant around 200–330 °C exists in both compositions. In wide temperature range below T_m, the frequency ν dependence of dielectric constant ε' of the new perovskite ceramics is well described by a formula $\varepsilon'(\nu) = \varepsilon'(1\,\mathrm{Hz}) - B\log\nu$ $(100\,\mathrm{Hz} \le \nu \le 1\,\mathrm{MHz})$.

Acknowledgment

This work was supported by the Fund of National Natural Science Foundation of China (Project No. 50272052).

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