Ceramics International 33 (2007) 95–99

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

# Piezoelectric and dielectric properties of $CeO_2$-doped $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ lead-free ceramics

Yueming Li [a,b], Wen Chen [a,*], Qing Xu [a], Jing Zhou [a],
Yan Wang [a], Huajun Sun [a]

[a] *Institute of Materials Science and Engineering, Wuhan University of Technology, Wuhan, Hubei 430070, PR China*
[b] *Jingdezhen Ceramic Institute, Jingdezhen, 333001, Jiangxi, PR China*

Received 24 January 2005; received in revised form 24 June 2005; accepted 22 August 2005

## Abstract

$CeO_2$-doped lead-free $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ piezoelectric ceramics (0–1.0 wt%) were synthesized by conventional ceramics technique. X-ray diffraction shows that $CeO_2$ diffuses into the lattice of $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ to form a solid solution, but does not change the rhombohedral phase in $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ during sintering. The temperature dependence of dielectric constant $\varepsilon_r$ and dielectric loss tan $\delta$ measurement reveals that the solid solutions experience two phase transitions from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric, which can be proved by $P$–$E$ hysteresis loops at different temperatures. The specimen containing 0.2 wt% $CeO_2$ shows that the coercive field $E_c$ decreases from 8.22 to 4.76 kV/mm while the remnant polarization $P_r$ decreases from 37.2 to 30.0 $\mu C/cm^2$, corresponding to the enhancement of piezoelectric constant $d_{33}$ of 132 pC/N and electromechanical coupling factor $k_p$ of 27.8%.

*Keywords:* A. Powders solid-state reaction; C. Piezoelectric properties; C. Dielectric properties; $Na_{0.5}Bi_{0.5}TiO_3$

## 1. Introduction

Lead oxide-based piezoelectric ceramics, represented by lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT) are widely used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [1]. However, volatilization of toxic PbO during high-temperature sintering not only causes environmental pollution, but also generates unstability of composition and electrical properties of products. Therefore, it is necessary to develop environment-friendly lead-free piezoelectric ceramics to replace the PZT-based ceramic, which has become one of the main trends in present development of piezoelectric materials.

Sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), is a kind of perovskite $ABO_3$-type ferroelectric discovered by Smolenskii et al. in 1960 [2]. NBT is considered to be an excellent candidate of lead-free piezoelectric ceramics to replace the lead-based piezoelectric materials because it is a strong ferroelectric with a large remnant polarization, $P_r = 38\ \mu C/cm^2$ [2]. It reveals a very interesting anomaly of dielectric properties as a result of a low-temperature phase transition from ferroelectric to anti-ferroelectric phase at 200 °C. However, this material has a drawback of high conductivity and high coercive field $E_c$ which cause problems in the poling process. To improve its properties, some modifications on NBT composition have been performed. It has been reported that NBT-based compositions modified with $K_{0.5}Bi_{0.5}TiO_3$ (KBT), $BaTiO_3$ (BT), $NaNbO_3$ (NN), $Bi_2O_3 \times Sc_2O_3$, or $La_2O_3$ showed improved piezoelectric properties and ease of poling compared with pure NBT ceramics [3–8]. Among them, NBT–KBT was more interesting owing to a good piezoelectric constant $d_{33} = 100$ pC/N [3,4]. It has been demonstrated that the maximum remnant polarization in NBT–KBT ceramics was located at 0.13 mol of KBT, and the solid solution shows a rhombohedral structure with a low dielectric constant $\varepsilon_{33}^T/\varepsilon_0$, a relatively high piezoelectric constant $d_{33}$ and a good electromechanical coupling factor $k_p$ [4]. In PZT ceramics, $CeO_2$ was an effective additive in enhancing its piezoelectric properties for it has two valence states of $Ce^{3+}$ and $Ce^{4+}$, respectively [1]. In this work, $CeO_2$ was selected as dopant to show its effect on improving the electrical properties of the

---

* Corresponding author. Tel.: +86 27 87642079; fax: +86 27 87864580.
*E-mail address:* chenw@public.wh.hb.cn (W. Chen).

0272-8842/$30.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.08.001

$Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ ceramics. The dielectric properties of $CeO_2$-doped $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ were also measured as a function of temperature. The modification mechanism of doped $CeO_2$ was also discussed.

## 2. Experimental

A conventional ceramic fabrication technique was adopted to synthesize $CeO_2$-doped $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ (abbreviated BNKT) ceramics. Reagent grade oxide or carbonate powders of $Bi_2O_3$, $Na_2CO_3$, $K_2CO_3$, $TiO_2$ and $CeO_2$ were used as starting raw materials. According to a composition of $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3 + x$ wt% $CeO_2$ ($x = 0, 0.1, 0.2, 0.4, 0.6, 0.8$ and 1.0 wt %), appropriate amount of raw materials were mixed using a planetary mill with agate media and ethanol for 6 h. After being mixed, the dried powders were calcined at 900 °C for 2 h. The calcined powder was reground by a planetary mill with agate media and ethanol for 10 h. The dried powder was mixed with polyvinyl alcohol and pressed with a pressure of 150 MPa into disks of 20 mm diameter and about 1.5 mm thick. After binder burnout, these pressed disks were sintered at 1150–1200 °C with 2-h soaking period in air. Silver paste was fired on both faces of the disks at 800 °C as electrodes. The specimens for measurement of piezoelectric properties were poled in silicon oil at 80 °C under 3–4 kV/mm for 15 min.

X-ray powder diffraction (XRD) patterns were taken on a D/MAX-III X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and graphite monochrometer. The diffraction data was recorded for $2\theta$ between 20 and 80° with a resolution of 0.02°. The relative dielectric constant $\varepsilon_r$ of unpoled ceramics at room and elevated temperatures was measured at 1, 10 and 100 kHz using a TH2816 LRC meter. The piezoelectric constant $d_{33}$ of the samples was measured by means of a quasi-static $d_{33}$ meter (ZJ-3A) based on the Berlincourt method at 110 Hz. The dielectric and piezoelectric properties were measured by means of the resonance–anti-resonance method using a precision impedance analyzer (HP4294A). The electromechanical coupling factor $K_p$ was calculated from the resonance and anti-resonance frequencies based on the Onoe's formula [9]. The $P$–$E$ hysteresis loops were obtained with a Radiant Precision Workstation. The microstructure of the sintered samples was observed with a scanning electron microscope (JSM-5610LV, Japan).

## 3. Results and discussions

### 3.1. Crystal structure

The X-ray diffraction patterns shown in Fig. 1 indicate that a solid solution with perovskite-type structure has been formed for all specimens, implying that $CeO_2$ diffused into the BNKT lattice during sintering. The lattice distortion in the $CeO_2$-doped BNKT solid solutions was investigated in the $2\theta$ range of 38–50°. The indices ($h$ $k$ $l$) of the reflecting planes of the $CeO_2$-doped BNKT were two peaks to (0 0 3)/(0 2 1) at about 39.8° and one peak to (202) at around 46.5° which indicates that all the specimens had rhombohedral symmetry structure. The lattice and angle parameter were indexed to be a rhombohedral symmetry structure, meaning that addition of $CeO_2$ does not lead to an obvious change in the phase structure.

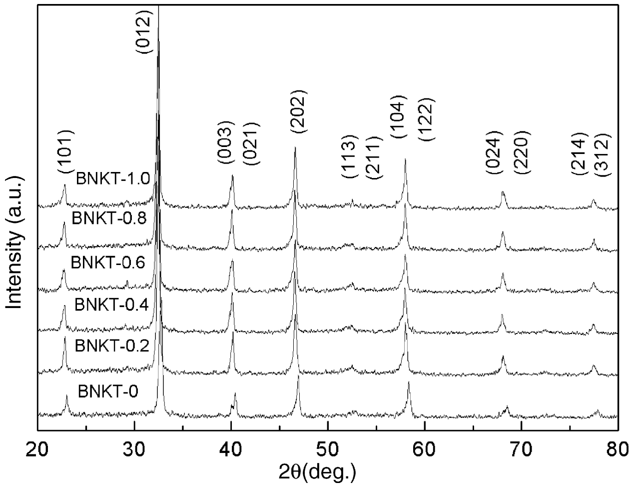

Fig. 1. XRD patterns of $CeO_2$-doped BNKT ceramics at room temperature.

### 3.2. Dielectric and ferroelectric property

Fig. 2 shows the temperature dependence of dielectric constant $\varepsilon_r$ of $CeO_2$-doped BNKT ceramics at 1 kHz between room temperature and 500 °C. Two peaks were observed to occur during the heating process, corresponding to the phase transitions from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric which was in accordance with our previous results [10]. Here, the transition temperature corresponding to the phase transition of ferroelectric to anti-ferroelectric phase is called the depolarization temperature ($T_d$) and the temperature corresponding to the maximum value of dielectric constant is named as maximum temperature ($T_m$). $T_m$ could be considered as the Curie point ($T_c$) because that $T_c$ corresponds to the transition between anti-ferroelectric and paraelectric phase. It was found that the dielectric constant at $T_m$ of $CeO_2$-doped ceramics was much higher than that of pure

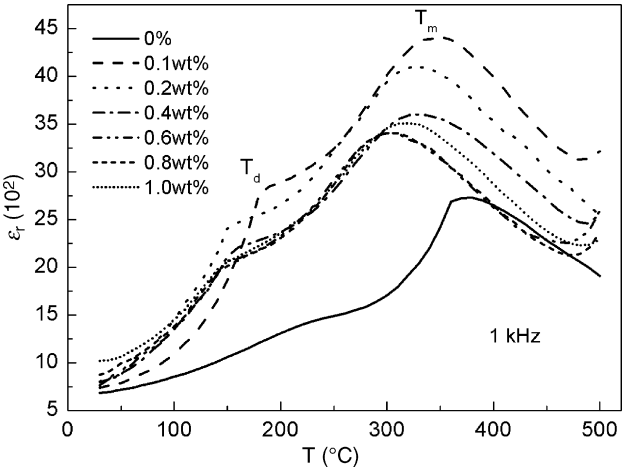

Fig. 2. Dielectric constant $\varepsilon_r$ as a function of temperature for 0–1.0 wt% $CeO_2$-doped BNKT ceramics at 1 kHz.

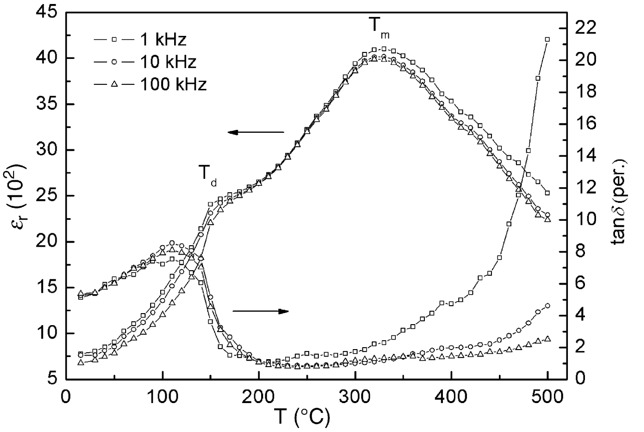

Fig. 3. The dielectric constant $\varepsilon_r$ and dielectric loss tan $\delta$ as a function of temperature for 0.2 wt% $CeO_2$-doped BNKT ceramic at 1, 10 and 100 kHz.

BNKT ceramics. However, the dielectric constant at $T_m$ decreased with increasing $CeO_2$ content. Also, it was noted that with the increase of $CeO_2$ content, the temperatures $T_m$ and $T_d$ decreased and the dielectric peaks gradually became broader. The temperature dependence of the dielectric constant $\varepsilon_r$ and the dielectric loss tan $\delta$ for 0.2 wt% $CeO_2$-doped BNKT ceramics were taken at measurement frequencies of 1, 10 and 100 kHz as shown in Fig. 3. It was found that the specimen presented relaxor characteristics, i.e. both dielectric constant $\varepsilon_r$, dielectric loss tan $\delta$, transition temperatures $T_d$ and $T_m$ were strongly frequency dependent, the higher the frequency, the lower the dielectric constant value and the higher the transition temperatures $T_d$ and $T_m$. It is thought that different ions randomly occupy the A- or B-site sublattice of $ABO_3$-type perovskite unit cell, which would form a numbers of chemical microregions with distinctive composition of the A- or B-site cations. Each microregion possesses its own Curie temperature ($T_c$), leading to relaxor characteristics [11]. In this work, the coexistence of $Na^+$, $K^+$ and $Bi^{3+}$ ions at the A-site may induce a relaxor ferroelectric behavior, which was also shown proved by Säid et al. [12]. Therefore, it can be concluded that the $CeO_2$-doped BNKT ceramics is still a relaxor ferroelectric.

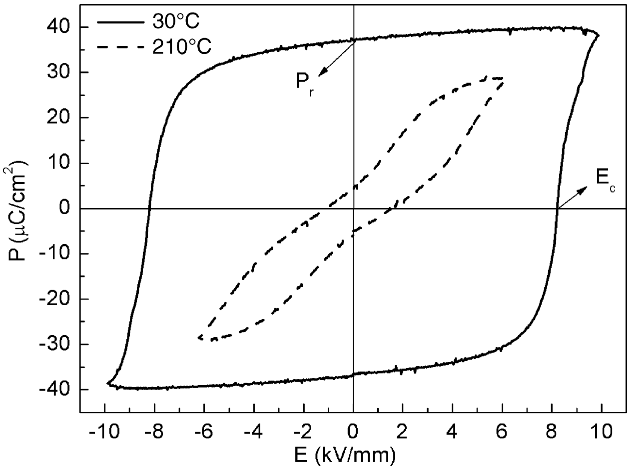

Fig. 4. P–E hysteresis loops of pure BNKT ceramic at 30 and 210 °C.

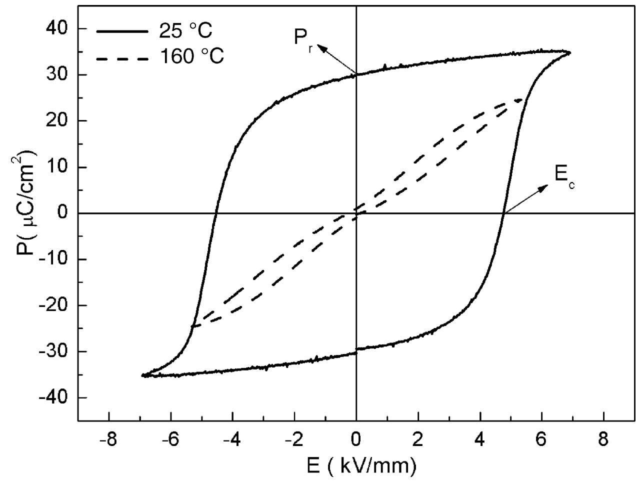

Fig. 5. P–E hysteresis loops of 0.2 wt% $CeO_2$-doped BNKT ceramic at 25 and 160 °C.

Figs. 4 and 5 depict the P–E hysteresis loops of pure BNKT and 0.2 wt% $CeO_2$-doped BNKT ceramics at room and at high temperature, respectively. It was observed that the remnant polarization $P_r$ decreases from 37.2 to 30.0 μC/cm$^2$ by doping 0.2 wt% $CeO_2$ at room temperature. The coercive field $E_c$ decreases more distinctly from 8.22 to 4.76 kV/mm. This result implies that the ferroelectric properties of BNKT would significantly be affected by doping with $CeO_2$. At 210 °C, the P–E hysteresis loop of pure BNKT ceramics became very narrow, which can be ascribed to an anti-ferroelectric phase. However, the BNKT containing 0.2 wt% $CeO_2$ also showed narrower double P–E hysteresis loops at lower temperature, revealing an obvious anti-ferroelectric feature. Thus it can be concluded that there exists a transition from ferroelectric to anti-ferroelectric phase for the specimens during heating.

### *3.3. Piezoelectric property*

Figs. 6 and 7 show the piezoelectric and dielectric properties of poled specimens for 0–1.0 wt% $CeO_2$-doped BNKT ceramics. It was found that with the addition of $CeO_2$ dopant,

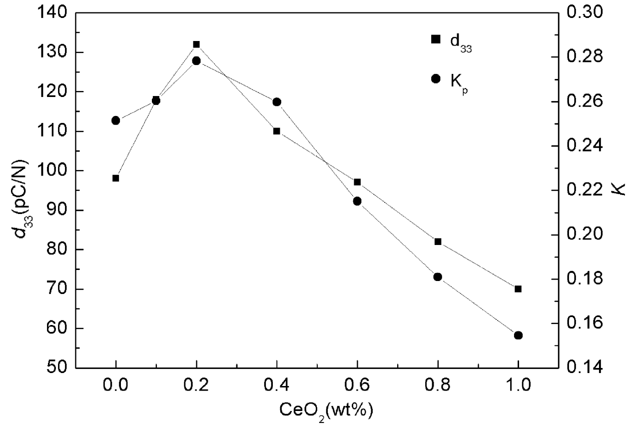

Fig. 6. The piezoelectric constant $d_{33}$ and electromechanical coupling factor $k_p$ as a function of amount of dopant $CeO_2$.

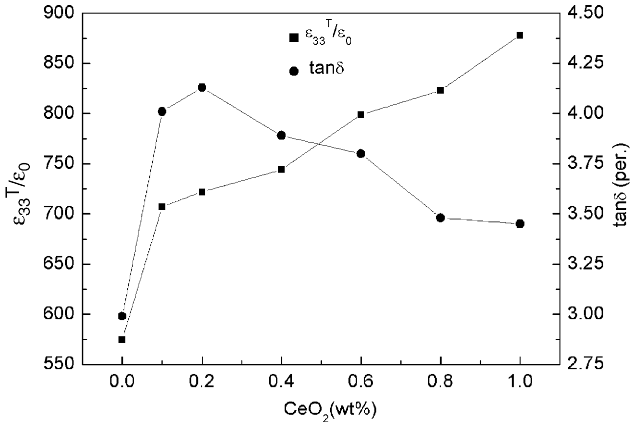

Fig. 7. The dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and dielectric loss tan $\delta$ as a function of amount of dopant $CeO_2$.

the piezoelectric constant $d_{33}$, the electromechanical coupling factor $k_p$ and the dielectric loss tan $\delta$ reached a maximum value at 0.2 wt% $CeO_2$ then decreased with more $CeO_2$ content. However, the dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ increased steadily. Similarly, at this doping level, the piezoelectric constant was altered from 98 pC/N for pure BNKT to 132 pC/N for the $CeO_2$-doped BNKT composition, and the electromechanical coupling factor $k_p$ was increased from 25.4 to 27.8%. It is well known that $CeO_2$ is a commonly used additive for PZT ceramics were it can generally improve the piezoelectric properties [1]. In this work, $CeO_2$ also showed the same effect. The mechanism for the effect of $CeO_2$ in this experiment is very complicated. Ce ion possibly exists in the BNKT structure in two valence states: $Ce^{4+}$ in radius of 0.92 Å and $Ce^{3+}$ in radius of 1.03 Å. In view of the radius, it is obvious that $Ce^{3+}$ cannot enter into the B-site of BNKT perovskite because the radius of $Ti^{4+}$ is 0.68 Å, but can occupy A-site. Here, there are two cases. One is that $Ce^{3+}$ goes to $Bi^{3+}$ site in BNKT. It is known that $Bi_2O_3$ is volatile at high temperature. During sintering, $Bi^{3+}$ in BNKT may leave the ceramic and form some vacancies in the lattice. It is possible for $Ce^{3+}$ to fill in $Bi^{3+}$ vacancies. However, $Bi^{3+}$ has a radius of 0.96 Å which is very close to 1.03 Å of $Ce^{3+}$ and 0.92 Å of $Ce^{4+}$. When $Ce^{3+}$ enters into the Bi-site of BNKT ceramics, the replacement of $Bi^{3+}$ by $Ce^{3+}$ almost does not cause the deformation in BNBT lattice to make an evident contribution to enhance the domain movement. However, $Ce^{4+}$ can also enter into the Bi-site. In this case, $Ce^{4+}$ functions as a donor leading to some vacancies of A-site in the lattice, which facilitates the movement of domain wall so as to improve the piezoelectric properties. Another one is that $Ce^{3+}$ and $Ce^{4+}$ occupy the A-site of $Na^+$ ($r_{Na^+} = 0.97$ Å) of BNKT composition which are the same with the $Ce^{4+}$ enter into $Bi^{3+}$. In these cases, many existing vacancies bring to defect in lattice which resulting in an increasing in the dielectric loss.

The microstructures of the sintered BNKT containing 0–1 wt% $CeO_2$ were observed by SEM, and micrographs of the samples with 0, 0.2, 0.4, 1 wt% $CeO_2$ are shown in Fig. 8. It is evident that $CeO_2$ addition causes a significant change in the grain size. It seems that $CeO_2$ addition prohibits from the grain growth. The grain size decreases with the increase in $CeO_2$ amount, especially, the morphologies of BNKT containing 1.0 wt% $CeO_2$ changed from sphericity to square pillar. Hence, the amount of $CeO_2$ in BNKT composition concerns a change in the grain size.

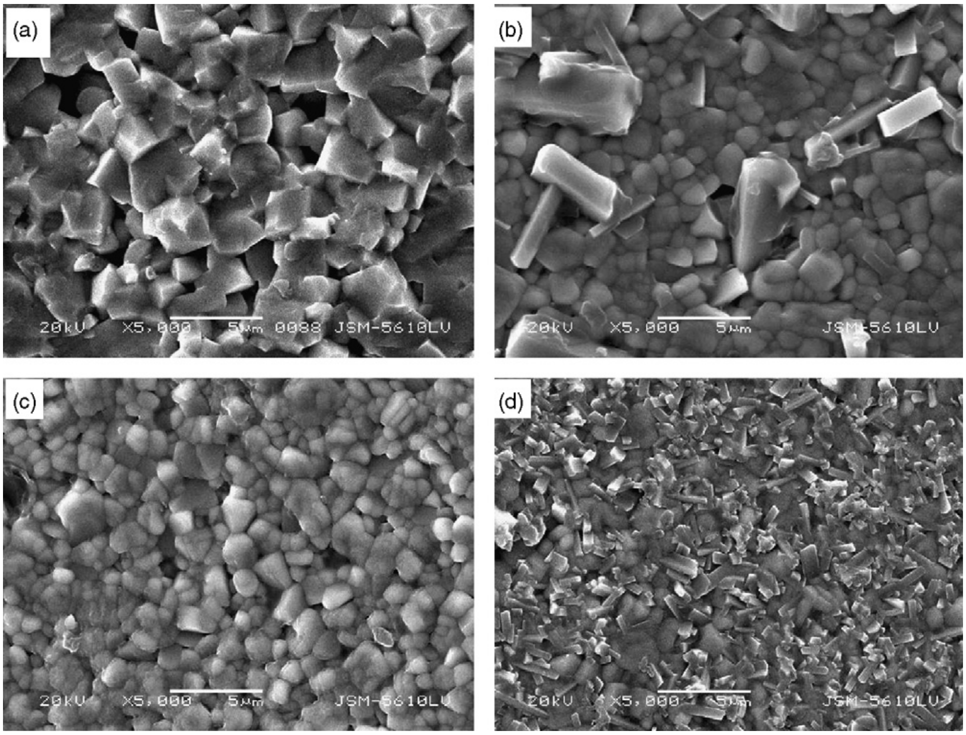

Fig. 8. Micrographs of $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ ceramics sintered at 1170 °C for 2 h with (a) 0, (b) 0.2, (c) 0.4 and (d) 1.0 wt% $CeO_2$.

## 4. Conclusions

With 0–1.0 wt% $CeO_2$-doped $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ ceramics can form pure perovskite-type solid solution with rhombohedral symmetry structure. All solid solution compounds experienced two phase transitions in the range of room temperature to 500 °C, i.e. from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric phase transition with relaxor characteristics. *P–E* hysteresis loops showed that the remnant polarization of 0.2 wt% $CeO_2$-doped $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ ceramic decreased from 37.2 to 30.0 $\mu C/cm^2$, meanwhile the coercive field $E_c$ decreased from 8.22 to 4.76 kV/mm. The piezoelectric constant $d_{33}$ and electromechanical coupling factor $k_p$ reached values of 132 pC/N and 27.8%, respectively.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 50272044), Natural Science Foundation of Hubei Province, China (Grant No. 2002AB076) and Nippon Sheet Glass Foundation for Materials Science and Engineering (Japan).

## References

[1] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic, New York, 1971.

[2] G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, N.N. Krainik, New ferroelectrics of complex composition, Sov. Phys. Solid State 2 (1961) 2651–2654.

[3] A. Sasaki, T. Chiba, Y. Mamiya, Y. Mamiya, E. Otsuki, Dielectric and piezoelectric properties of $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ system, Jpn. J. Appl. Phys. 38 (1999) 5564–5567.

[4] T.B. Wang, L.E. Wang, Y.K. Lu, D.P. Zhou, Electro-physical properties of ceramics of $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ system in Na-rich region, J. Chin. Ceram. Soc. 14 (1986) 14–22 (in Chinese).

[5] T. Takenaka, K. Maruyama, K. Sakata, $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ system for lead-free piezoelectric ceramics, Jpn. J. Appl. Phys. 30 (9B) (1991) 2236–2239.

[6] T. Takenaka, T. Okuda, K. Takegahara, Lead-free piezoelectric ceramics based on $Na_{1/2}Bi_{1/2}TiO_3$–$NaNbO_3$, Ferroelectrics 196 (1997) 175–178.

[7] H. Nagata, T. Takenaka, Lead-free piezoelectric ceramics of $Na_{1/2}Bi_{1/2}TiO_3$–1/2($Bi_2O_3 \times Sc_2O_3$) system, Jpn. J. Appl. Phys. 36 (1997) 6055–6057.

[8] A. Herabut, A. Safari, Processing and electromechanical properties of $(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$ ceramics, J. Am. Ceram. Soc. 80 (11) (1997) 2954–2958.

[9] M. Onoe, H. Juumonji, Useful formulas for piezoelectric ceramic resonators and application to measurement of parameters, J. Acoust. Soc. Am. 47 (1967) 974–980.

[10] Y.M. Li, W. Chen, J. Zhou, Q. Xu, H.J. Sun, M.S. Liao, Dielectric and ferroelectric properties of lead-free $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ ferroelectric ceramics, Ceram. Int. 31 (2005) 139–142.

[11] G.A. Smolenskii, Physical phenomena in ferroelectrics with diffuse phase transition, Jpn. J. Phys. Soc. 28 (Suppl.) (1970) 26–37.

[12] S. Säid, J.P. Mercurio, Relaxor behavior of low lead and lead-free ferroelectric ceramics of the $Na_{0.5}Bi_{0.5}TiO_3$–$PbTiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$system, J. Eur. Ceram. Soc. 21 (2001) 1333–1336.