

Electrical and microstructural properties of CaTiO_3 -doped $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ -lead free ceramics

L RAMAJO*, R PARRA, M A RAMÍREZ[†] and M S CASTRO

Institute of Research in Materials Science and Technology (INTEMA), (CONICET – Universidad Nacional de Mar del Plata), Juan B Justo 4302 (B7608FDQ), Mar del Plata, Argentina

[†]Faculdade de Engenharia de Guaratinguetá (FEG), Universidade Estadual Paulista (UNESP), Av. Dr. Ariberto Pereira da Cunha, 333, Bairro Pedregulho, CEP 12516-410, Guaratinguetá, SP, Brazil

MS received 12 January 2011; revised 28 February 2011

Abstract. Microstructure, electrical properties and dielectric behaviour of $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (KNN) and CaTiO_3 -modified $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (CTO-KNN) systems, were investigated. Discs doped with 0 to 0.55% mol of CaTiO_3 (CTO) were sintered at 1125°C for 2 h. Although minority phases were found in doped samples, CaTiO_3 was not detected. It was also observed that CTO changed the microstructure and grain size of KNN drastically. Also, the Curie temperature and permittivity values decreased. Addition of CTO between 0.15 and 0.45 mol% decreases the density and dielectric values. Samples prepared with higher content of CTO than 0.45 mol% showed better electrical properties.

Keywords. $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$; CaTiO_3 ; lead-free ceramics; electrical properties.

1. Introduction

Lead zirconate titanate (PZT) ceramics are widely used in piezoelectric transducers, transformers and sensors due to their superior dielectric, ferroelectric and piezoelectric properties (Du *et al* 2005; Yang *et al* 2005; Chang *et al* 2006). Nevertheless, due to the toxicity and its high vapour pressure during the sintering process, lead is a serious threat to human health and environment. Therefore, in recent years lead-free piezoelectric ceramics have attracted great attention.

A number of researches on lead-free piezoelectric ceramics such as alkaline niobate (Saito *et al* 2004; Matsubara *et al* 2005), BaTiO_3 -based (Yu *et al* 2002), Bi-layered (Sawada *et al* 2003), bismuth sodium titanate (Zhou and Xin 2007; Zhou *et al* 2009) and tungsten bronze-type materials (Suzuki *et al* 2003) have been recently published. In this way, niobates $(\text{K},\text{Na})\text{NbO}_3$ (KNN)-based ceramics have showed good piezoelectric and electric properties, high Curie temperature and environmental innocuity (Maeder *et al* 2004; Wang *et al* 2004; Alkoy and Papila 2010). Also, when the ratio of K/Na reaches 50/50, the piezoelectric coefficient reaches the highest point (up to 80 pC/N) (Ringgaard and Wurlitzer 2005). Nevertheless, because of the high volatility of alkaline metals at high temperature and its hydrophilic feature, it is very difficult to obtain dense and well-sintered KNN ceramics using conventional sintering processes.

A variety of modifications have been attempted to prepare new KNN-based ceramics with improved density and

piezoelectric properties, such as KNN– LiSbO_3 (Tang *et al* 2007; Wang *et al* 2008) and KNN– LiNbO_3 (Wu *et al* 2007). The improved piezoelectric properties of these ceramics could be due to the polymorphic phase transition (PPT) near or at room temperature (Bobnar *et al* 2004; Wang *et al* 2008; Wu *et al* 2008a), even though it has been found that these KNN systems possess low-temperature stability for PPT near to or at room temperature (Wu *et al* 2008b). This low-temperature stability restricts the practical applications of KNN-based ceramics. It would, therefore, be useful to obtain KNN-based ceramics with good temperature stability along with high piezoelectric properties for practical applications.

In this work, $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (KNN) and CaTiO_3 – $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (CTO–KNN) ceramics were prepared by a conventional sintering technique. The microstructure, dielectric and ferroelectric properties of these ceramics were studied.

2. Experimental

Lead-free potassium sodium niobate, $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (KNN), was produced by the conventional solid state reaction method from potassium carbonate (Biopack 99.5%, Argentina), sodium carbonate (Cicarelli 99.7%, Argentina) and niobium oxide powder (Aldrich 99.9%, USA). Powders with K:Na = 1:1 and different CaTiO_3 (CTO) concentrations ($x = 0.15, 0.25, 0.45$ and 0.55 mol%) were mixed and milled in 2-propanol in a planetary laboratory ball-mill (Fritsch, Pulverisette 5) with zirconia balls for 6 h at 1000 rpm using a ball-to-powder mass ratio of 7:10. Afterwards, the resulting powders were calcined at 900°C for 5 h in air.

*Author for correspondence (lramajo@fi.mdp.edu.ar)

Powders were milled for a second time in a planetary laboratory ball-mill (Fritsch, Pulverisette 5) with zirconia balls for 30 min. This step reduced the particle size, which is necessary to achieve a good dispersion and compaction. Then, the resulting powders were uniaxially pressed into discs of 6 mm in diameter and 0.5 mm in thickness. The obtained discs were sintered at 1125°C for 180 min in a conventional furnace with 5°C/min heating and cooling rates under ambient atmosphere.

The crystalline phases were assessed by X-ray diffraction using a Philips PW1050/25 diffractometer running with CuK_α radiation, at 40 kV and 30 mA. The samples were examined by scanning electron microscopy (SEM), using a JEOL JSM-6460LV microscope.

Silver electrodes were painted on the surface of the sintered samples for electrical measurements. Dielectric spectroscopy measurements were carried out with a frequency response analyser HP 4284A LCR meter in the 20 Hz to 1 MHz frequency range. Polarization vs electric field hysteresis loops were obtained at room temperature by applying an electric field of sinusoidal waveform at a frequency of 50 Hz by means of a modified Sawyer–Tower bridge with the sample inside a silicone oil bath.

3. Results and discussion

3.1 XRD and SEM characterization

Figure 1 shows the X-ray diffraction patterns of KNN doped with different concentrations of CTO (0 to 0.55 mol%) after sintering at 1125°C for 120 min in air. The diffraction peaks could be clearly indexed to a perovskite with orthorhombic structure of KNN (Malic *et al* 2005; Birol *et al* 2006). Also, traces of secondary phases were detected, which could be $(\text{Na, K})\text{Nb}_8\text{O}_{21}$ (Malic *et al* 2005) or other alkaline niobates like NaNb_3O_8 or K_3NbO_4 (JCPDS 84–1432 and 23–1345). CTO phase was not observed; probably due to problems to keep a stable structure inside KNN, since both have the same ABO_3 perovskite structure, or due to homogeneous distribution. Moreover, the addition of CTO induced a phase diffusion transition between an orthorhombic phase and a weak tetragonal phase.

Figure 1(B) shows enlarged XRD patterns between 44.75 and 46.5. It can be seen that crystal structure of undoped KNN exhibited an orthorhombic structure with the splitting of (202) and (020) characteristic peaks at $2\theta \sim 45.5^\circ$. However, this phase decreases with increasing CTO content. In this way, the crystal structure of samples with higher doping level revealed a clear evolution of the system toward a tetragonal structure. This phenomenon indicates that the orthorhombic and tetragonal phases coexist in KNN ceramics with a small amount of CTO.

The microstructural evolution of KNN as a function of CTO concentration is shown in the scanning electron microscopy images of figure 2. Undoped or doped samples

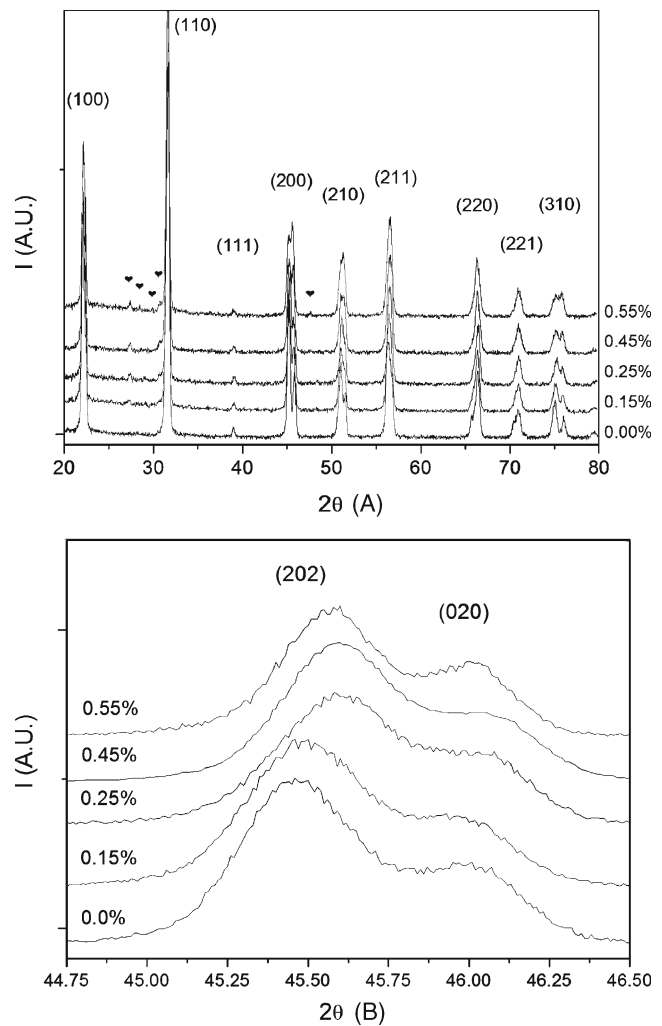


Figure 1. XRD patterns of KNN undoped (0%) and 0.15 to 0.55 mol% CTO-doped samples. (♥ Secondary phases (A)). Inset shows magnified patterns in the 44.75 to 46.5 2θ range (B).

with 0.15 mol% CTO exhibited similar grain size, shape and porosity, although both (size and shape) changed dramatically with increasing CTO content. Specimens with 0.25 and 0.45 mol% showed cubic, bigger grains with smooth faces. Additionally, these samples also presented lower density values (table 1). On the other hand, specimens doped with 0.55 mol% showed higher density with elongated grains.

3.2 Dielectric and electric characterization

NaNbO_3 phase is known as an antiferroelectric perovskite-type compound and possesses many phase transitions between -100 and 643°C . However, when it is combined with a ferroelectric phase like KNbO_3 , a new ferroelectric phase is produced with two phase transitions around 200 and 430°C , corresponding to the transition temperatures of orthorhombic to tetragonal and tetragonal (ferroelectric) to cubic (paraelectric) phases, respectively (Chang *et al* 2007a).

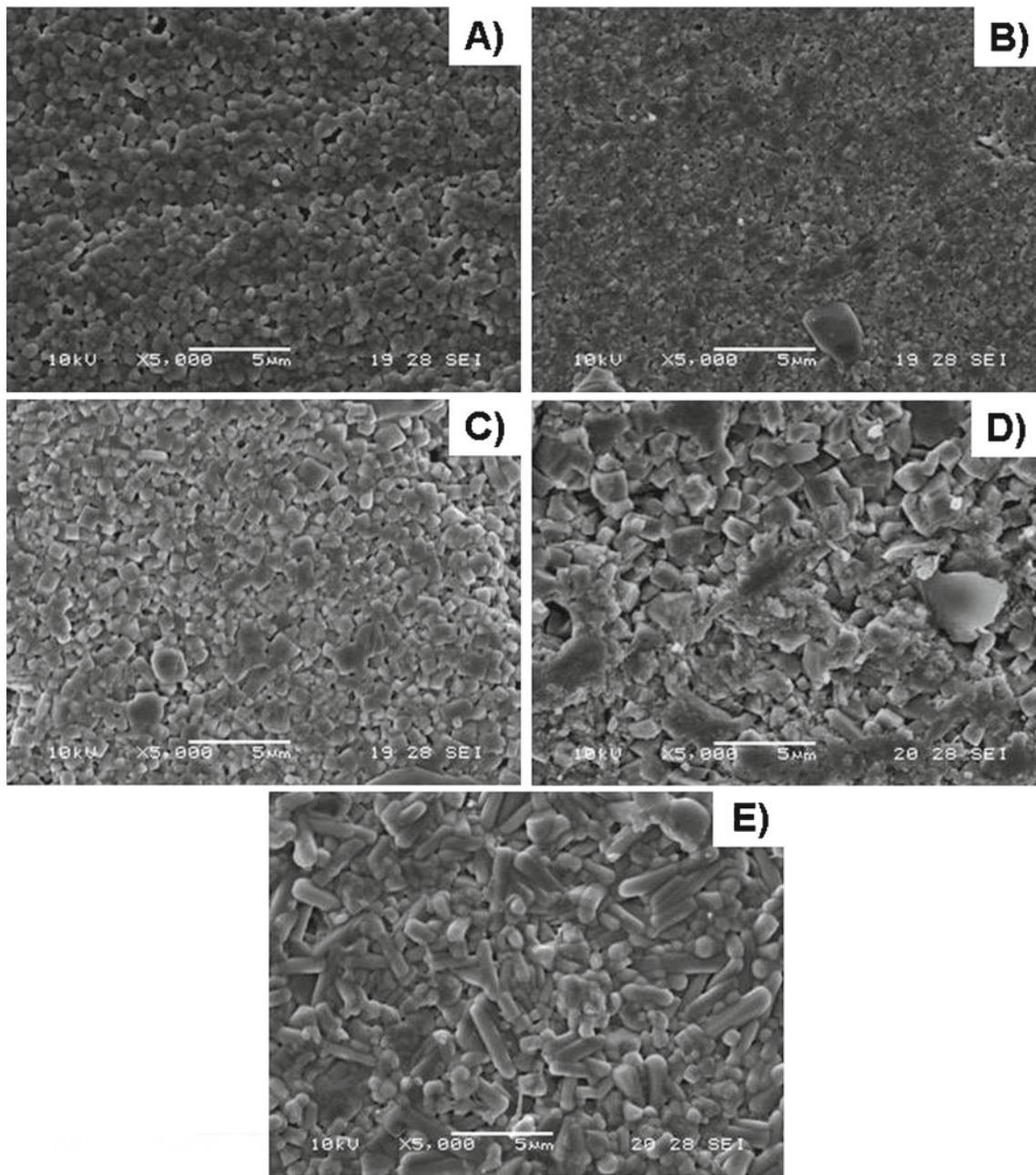


Figure 2. SEM images of undoped (A) and 0.15 (B), 0.25 (C), 0.45 (D) and 0.55 mol% (E) CTO-doped KNN samples.

Table 1. Density (ρ), porosity, dielectric properties (ϵ_r , $\tan \delta$), Curie temperature (T_C) and remnant polarization (P_r) of CTO doped KNN prepared by mixed oxide routes.

Content of CTO (mol%)	ρ (g/cm ³)	Porosity (%)	ϵ_r (at 10 kHz)	$\tan(\delta)$ (at 10 kHz)	T_C (°C)	P_r ($\mu\text{C}/\text{cm}^2$)
0.00	4.28 ± 0.1	5.47 ± 2.3	517.25	0.060	400	7.12
0.15	4.27 ± 0.1	5.51 ± 1.1	401.26	0.093	350	7.07
0.25	4.02 ± 0.1	12.76 ± 2.1	421.76	0.497	–	–
0.45	3.99 ± 0.1	16.49 ± 6.9	434.34	0.201	–	–
0.55	4.29 ± 0.1	5.06 ± 1.8	670.77	0.088	315	10.83

Dielectric properties of KNN and CTO-doped KNN (0.15 and 0.55 mol%), as a function of temperature at 10 kHz are shown in figure 3. Pure KNN ceramics show two-phase transition temperatures: the orthorhombic–tetragonal polymorphic phase transition (T_{o-t}) and the tetragonal–cubic ferroelectric–paraelectric phase transition (Curie temperature, T_C). It is observed that the transition temperatures and permittivity decrease when the CTO content is increased (Chu *et al* 2003; Chang *et al* 2006). Also, the real permittivity peaks at T_C were sharp and the highest values correspond to the undoped sample. Addition of 0.55 mol% shifted T_{o-t} close to room temperature. This phenomenon has been found in other compounds such as (Pb, La)(Zr, Ti)O₃ and doped BaTiO₃ (Guo *et al* 2004; Kosec *et al* 2004). It is suggested that a transition from a normal ferroelectric to ‘relaxor-like’ ferroelectric is due to the cation disorder in perovskite unit cell and the formation of microdomain since non-ferroelectric materials are added (Chang *et al* 2007b).

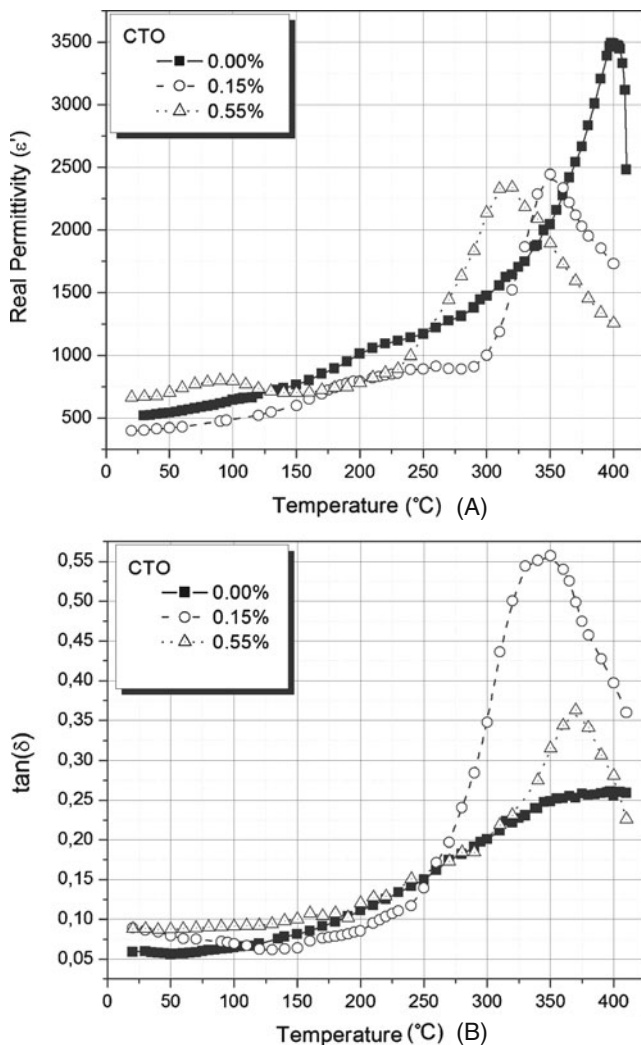


Figure 3. Variation of (A) real part of permittivity and (B) loss tangent ($\tan \delta$) as a function of temperature of 0, 0.15 and 0.55 mol% CTO-doped KNN (at 10 kHz).

It is known that the Curie temperature of CTO is negative (Chandra *et al* 2006), and exhibits quantum paraelectric phase at room temperature or higher. In this way, in table 1, the real permittivity and loss tangent are shown at room temperature as a function of CTO concentration at 10 kHz. The lower real permittivity value belongs to samples doped with 0.15 mol% of CTO, after that it begins to increase. The loss tangent of CTO-doped KNN increases with increasing CTO content up to 0.45%mol, returning to values similar to undoped samples with a CTO concentration of 0.55 mol%.

Finally, specimens with lowest porosity (0, 0.15 and 0.55 mol% of CTO), were analysed under an external strong electric field, exhibiting in all cases ferroelectric behaviour due to spontaneous polarization. Hysteresis loops of pure and doped-KNN with 0.15 and 0.55 mol% of CTO at room temperature under an a.c. electric field of $E_p = 40$ kV/cm at 50 Hz are shown in figure 4. Pure KNN shows a remnant polarization (P_r) of $7.12 \mu\text{C}/\text{cm}^2$, slightly higher than the value measured for the 0.15 mol% CTO doped-KNN, but lower than the measured one for the 0.55 mol% CTO doped-sample (7.07 and $10.83 \mu\text{C}/\text{cm}^2$, respectively). In this way, the coercive field E_c values of doped-KNN ceramics with 0, 0.15 and 0.55 mol% of CTO are 15.8, 16.7 and 13.5 kV/cm and the higher saturation values (P_s) are 13.21, 12.96 and $16.54 \mu\text{C}/\text{cm}^2$, respectively. Pure and doped KNN with 0.15 mol% of CTO show almost equal standards due to the comparable grain size, microstructure, dielectric permittivity and density, while the 0.55 mol% doped-sample showed the highest values. This can be attributed to a diffuse phase transformation between an orthorhombic phase and a weak tetragonal phase, the higher dielectric permittivity and average grain size of 0.55 mol% doped-KNN ceramic.

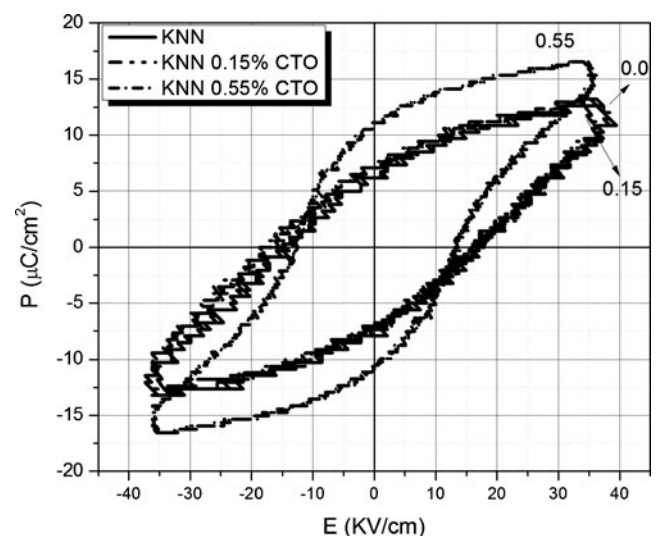


Figure 4. Hysteresis loops of 0, 0.15 and 0.55 mol% CTO-doped KNN at room temperature. Measuring conditions: a.c. field, electric field of 40 kV/cm and frequency of 50 Hz.

4. Conclusions

The effect of CTO (0 to 0.55 mol %) on the microstructure, phase transition and electric properties of KNN systems prepared by the conventional mixed oxide method has been studied. X-ray diffraction patterns showed the formation of a solid solution of CTO in KNN with perovskite-type structure. The average grain size, transition temperatures and real permittivity at room temperature were modified by the increasing CTO content.

The temperature dependence of real permittivity revealed that the examined samples showed a diffuse phase transition character and this character was more obvious with increasing concentration of CTO.

Small additive quantized slightly modified the properties, even though highest values decreased density and electric properties up to CTO 0.45 mol%. After that, the properties (density, and real permittivity) improved up to values similar to undoped ceramics. In this way, the results of this study suggest that KNN doped with 0.55 mol% of CTO would be a good candidate for ferroelectric devices.

Acknowledgements

The authors are grateful to CONICET and ANCyPT (Argentina) and to CNPq and FAPESP (Brasil) for the financial support provided for this research.

References

- Alkoy E M and Papila M 2010 *Ceram. Int.* **36** 1921
- Birol H, Damjanovic D and Setter B 2006 *J. Eur. Ceram. Soc.* **26** 861
- Bobnar V, Bernard J and Kosec M 2004 *Appl. Phys. Lett.* **85** 994
- Chandra A, Ranjan R, Singh D P, Khare N and Pandey D 2006 *J. Phys. Condens. Matter* **18** 2977
- Chang R-C, Chu S-Y, Lin Y-F, Hong C-S, Kao P-C and Lu C-H 2007a *Sensors Actuator* **A138** 355
- Chang R-C, Chu S-Y, Lin Y-F, Hong C-S and Wong Y-P 2007b *J. Eur. Ceram. Soc.* **27** 4453
- Chang Y, Yang Z, Wei L and Liu B 2006 *Mater. Sci. Eng.* **A437** 301
- Chu S Y, Water W, Juang Y D, Liaw J T and Dai S B 2003 *Ferroelectrics* **287** 23
- Du H, Qu S, Che J, Liu Z, Wei X and Pei Z 2005 *Mater. Sci. Eng.* **A393** 36
- Guo Y, Kakimoto K and Ohsato H 2004 *Solid State Commun.* **129** 279
- Kosec M, Bobnar V, Hrovat M, Bernard J, Malic B and Holc J 2004 *J. Mater. Res.* **19** 1849
- Maeder M D, Damjanovic D and Setter N 2004 *J. Electroceram.* **13** 385
- Malic B, Bernard J, Holc J, Jenko D and Kosec M 2005 *J. Eur. Ceram. Soc.* **25** 2707
- Matsubara M, Yamaguchi T, Sakamoto W, Kikuta K, Yogo T and Hirano S 2005 *J. Am. Ceram. Soc.* **88** 1190
- Ringgaard E and Wurlitzer T 2005 *J. Eur. Ceram. Soc.* **25** 2701
- Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T and Nakamura M 2004 *Nature* **432** 84
- Sawada T, Ando A, Sakabe Y, Damjanovic D and Setter N 2003 *Jpn. J. Appl. Phys.* **42** 6094
- Suzuki M, Nagata H, Ohara J, Funakubo H and Takenaka T 2003 *Jpn. J. Appl. Phys.* **42** 6090
- Tang F S, Du H L, Liu D J, Luo F and Zhou W C 2007 *J. Inorg. Mater.* **22** 0323
- Wang K, Li J and Liu N F 2008 *Appl. Phys. Lett.* **93** 092904
- Wang X, Kwork K, Tang X, Chan H and Choy Z 2004 *Solid State Commun.* **129** 319
- Wu J G, Xiao D, Wang Y, Zhu J, Yu P and Jiang Y 2007 *J. Appl. Phys.* **102** 114113
- Wu J G, Xiao D Q, Wang Y Y, Zhu J G and Yu P 2008a *J. Appl. Phys.* **103** 024102
- Wu J, Xiao D, Wang Y, Wu W, Zhang B, Li J and Zhu J 2008b *Scr. Mater.* **59** 750
- Yang Z P, Chang Y F and Li H 2005 *Mater. Res. Bull.* **40** 2110
- Yu Z, Ang C, Guo R and Bhalla A S 2002 *J. Appl. Phys.* **92** 1489
- Zhou C-H and Xin X-Y 2007 *Bull. Mater. Sci.* **30** 575
- Zhou C-H, Liu X-Y, Li W-Z and Yuan C-L 2009 *Bull. Mater. Sci.* **32** 99