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Effects of A-Site (NaCe) Substitution with Na-Deficiency on Structures and Properties of $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ -Based High-Curie-Temperature Ceramics

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Three kinds of bismuth-layer-structured ferroelectric (BLSF) ceramics, $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBT), $\text{Ca}_{0.8}(\text{CeNa})_{0.1}\text{Bi}_4\text{Ti}_4\text{O}_{15}$ (CNBT), and Na-deficient $\text{Ca}_{0.8}(\text{Ce}_{0.1}\text{Na}_{0.05}\square_{0.05})\text{Bi}_4\text{Ti}_4\text{O}_{15}$ [CN□BT] (where □ represents vacancies) were prepared by a conventional ceramic technique. X-ray powder diffraction showed that their crystal structures are a single phase of BLSF with $m = 4$. Sintering characteristics of the three ceramics were also discussed. Scanning electron microscope (SEM) micrographs of CN□BT showed that the grain is platelike. The A-site (NaCe) substitution can improve the piezoelectric constant d_{33} and high-temperature resistivity with decreasing Curie temperature. The modification by A-site (NaCe) substitution with Na-deficiency is more pronounced than CNBT, which not only leads to a very high piezoelectric constant d_{33} and high-temperature resistivity but also increases the Curie temperature. The reason for the high T_c ($T_c = 866^\circ\text{C}$) of CN□BT is considered to be internal stress. As a result, Na-deficient CN□BT ceramic is found to be an excellent high-temperature piezoelectric material.

KEYWORDS: bismuth-layer-structured ferroelectric, deficiency, substitution, high Curie temperature, piezoelectric constant, high-temperature resistivity

1. Introduction

The general formula for bismuth-layer-structured ferroelectrics (BLSFs) is $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ where A is a mono-, di-, or trivalent ion or a mixture of the three allowing dodecahedral coordination, B is a combination of cations well suited for octahedral coordination, and m is an integer usually lying in the range of 1–5.^{1,2)} The structure of these compounds can be regarded as a regular intergrowth of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ perovskite-type layers. In recent years, BLSFs have been given much attention³⁾ because BLSFs, such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT),⁴⁾ seem to be an excellent candidate material for nonvolatile ferroelectric random access memory (FRAM) in various commercial applications. The BLSF family is also attractive from an application viewpoint for electronic materials because BLSFs are characterized by (1) low dielectric constants, (2) high Curie temperature, (3) low temperature coefficients of the resonance frequency, (4) strong anisotropic electromechanical coupling factors, and (5) low ageing rate. Based on these characteristics, BLSF ceramics can be used as piezoelectric materials to be operated at high temperatures and at high frequencies with large figures of merit.^{2,5)}

However, the piezoactivity of BLSF is rather low. In order to overcome this disadvantage, a modification by stoichiometric amount substitutions was carried out. Usually, the T_c of BLSF modified by substitutions decreased while the piezoactivity improved.^{1,6)} However, no modification that can cause a simultaneous increase of T_c and d_{33} has been reported to date.

In the present work we examine the effects of A-site (NaCe) substitution with Na-deficiency on the structures and properties of BLSF $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ -based high Curie temperature ceramics. The material has a high value of T_c and fairly good piezoactivity.

2. Experimental Procedure

Ceramic samples of $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ [CBT], $\text{Ca}_{0.8}(\text{CeNa})_{0.1}\text{Bi}_4\text{Ti}_4\text{O}_{15}$ [CNBT], and Na-deficient $\text{Ca}_{0.8}(\text{Ce}_{0.1}\text{Na}_{0.05}\square_{0.05})\text{Bi}_4\text{Ti}_4\text{O}_{15}$ [CN□BT] (where □ represents vacancies) were prepared by the conventional ceramic technique.

The starting raw materials were Bi_2O_3 of 99.99% purity, $\text{Ca}(\text{OH})_2$ of 93% purity, TiO_2 of 99.02% purity, Na_2CO_3 of 99.8% purity, and CeO_2 of 99.9% purity. The materials, mixed by ball milling, were calcined at 820°C for 2 h. After calcination, the ground and ball-milled powders were pressed into disks and bars. The samples were sintered at $1100\text{--}1225^\circ\text{C}$ for 1 h in air. Electrodes for dielectric, piezoelectric, and resistivity measurements were fabricated using fired palladium paste.

Phase assemblages were characterized by X-ray diffraction using a Guinier-Hägg camera with $\text{Cu K}\alpha_1$ radiation and Si as an internal standard. The measurement of X-ray film and refinement of lattice parameters were completed by a computer-linked line scanner (LS-18) system⁷⁾ and SCANPI, PIRUM program.⁸⁾ Microstructures in the ceramic samples were observed using a scanning electron microscope (SEM). The temperature dependence of the dielectric constant and dielectric loss tangent $\tan \delta$ was measured on ceramic disks at a frequency of 1 kHz with a measuring field of about 1 V/mm using an automated dielectric measurement system with an LCR meter (Tonghui Electric TH2817) in the temperature range from room temperature to 900°C . Measurements were performed with increasing temperature. The rate of heating was about $1^\circ\text{C}/\text{min}$ in the vicinity of the transition temperature. Hysteresis loops were measured by an RT-6000 HVS instrument. Temperature dependence of the resistivity ρ was measured by a high resistance meter (Shanghai No. 6 Electric Meter Factory ZC43) in the temperature range from 100 to 500°C . The resistivity measurements were carried out under an electric field strength of 10 V/mm. Samples for piezomeasurements were poled in silicone oil at various temperatures (from 180 to 220°C) and under various DC electric field strengths (from 5 kV to 15 kV/mm), for 5 to 25 min. Piezoelectric measurements were conducted by the resonance-antiresonance method according to the IRE standard. Piezoelectric constant d_{33} was measured by a quasi-static d_{33} meter (Institute of Acoustics, Academia Sinica, ZJ-2).

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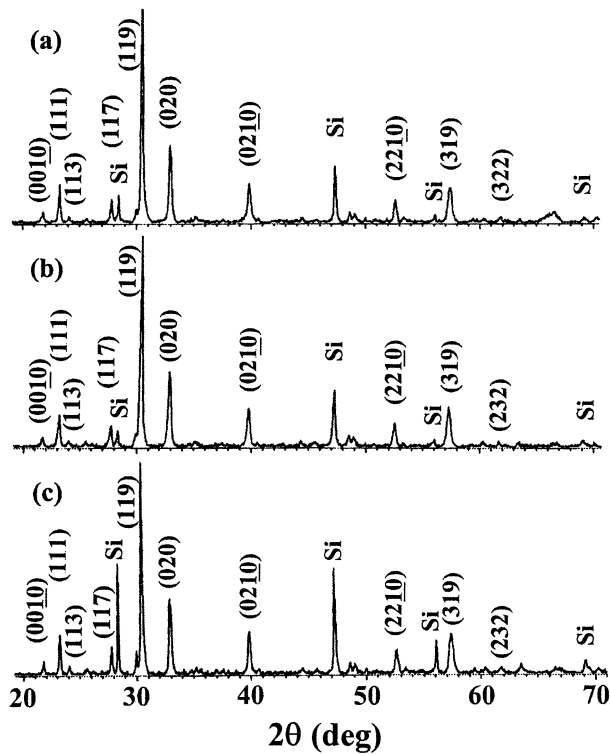


Fig. 1. X-ray powder diffraction patterns of (a) CBT, (b) CNBT, and (c) CN□BT.

3. Results and Discussion

Figure 1 shows X-ray powder diffraction patterns of (a) CBT, (b) CNBT, and (c) CN□BT. The patterns of CNBT and CN□BT are almost the same as that of CBT. Because CBT belongs to the BLSF family,⁹⁾ the diffraction patterns of CNBT and CN□BT indicated an almost single phase of BLSF with $m = 4$. The X-ray diffraction data were indexed on the basis of an orthorhombic symmetry. From these patterns, the orthorhombic lattice constants were calculated using the least squares method. After A-site (NaCe) substitution, the orthorhombic lattice parameters a , b , and c and the cell volume V of CNBT are smaller than those of CBT. After A-site (NaCe) substitution with Na-deficiency, the lattice parameters a , b , and c and the cell volume V of CN□BT are larger than those of CNBT. Thus the expansion of unit cell volume V of CN□BT means that the lattice distortion caused by A-site vacancies causes tensile stress in the cell, which obstructs the shrinkage of the a -axis (spontaneous polarization axis) in ferroelectric-paraelectric phase transition. The lattice parameters of CBT, CNBT and CN□BT are given in Table I.

Figure 2 shows the sintering characteristics of the three ceramics. The left vertical axis is the relative density, that is, the ratio of the sample density to the theoretical X-ray density. The theoretical X-ray density was obtained using the lattice

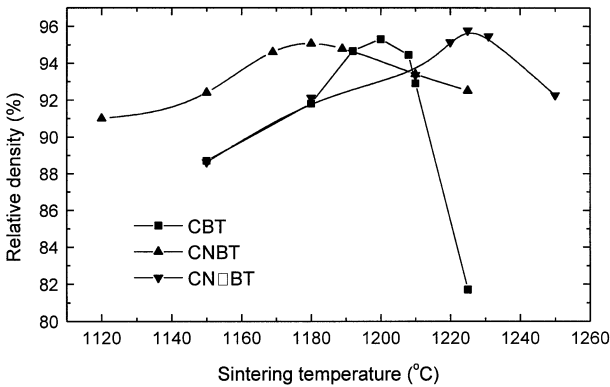


Fig. 2. Relative density of the three ceramics.

parameters listed in Table I. After A-site substitution, the optimum sintering temperature of CNBT is lower than that of CBT, but the maximum relative density decreases. The maximum relative density of Na-deficient CN□BT is the highest among the three ceramic materials, and the optimum sintering temperature of CN□BT is also higher than that of the other two ceramics.

Figure 3 shows the SEM micrographs of the natural surface of CN□BT fired at various temperatures. The grain growth is structurally highly anisotropic. The grains in the fired sample are platelike, which is characteristic of BLSF ceramics.^{10,11)} The average length l and thickness t of the platelets differ at different sintering temperatures. The ratio of l/t increases with increasing sintering temperature.

Figure 4 shows the temperature dependence of the resistivity ρ of the three materials. The resistivity decreases with increasing temperature. Below 285°C, the resistivity of CBT is higher than those of CNBT and CN□BT. However, above 285°C, the resistivity of CN□BT becomes the highest among the three materials. The high-temperature resistivity of CN□BT is larger than $1.59 \times 10^7 \Omega \cdot \text{cm}$ when the measurement temperature is 500°C. However the high-temperature resistivity of CBT at 500°C is only $1.6 \times 10^6 \Omega \cdot \text{cm}$. Obviously, the modification improved the high-temperature resistivity of CBT-based ceramics, which is important for their use as high-temperature piezoelectric devices.

Figure 5 shows the hysteresis loops of the three compounds observed at room temperature. It is well known that BLSF has a higher coercive field than other conventional piezoceramics,²⁾ thus a high-temperature poling process is necessary in order to activate the piezoceramics because the coercive field E_c decreases as the temperature rises. Table II shows the piezoelectric and dielectric properties of CBT, CNBT and CN□BT. After substitution, the piezoelectric constant d_{33} and the electromechanical coupling factor k_{33} show an obvious increase compared with those of CBT. However the d_{33} value measured by the d_{33} meter is clearly higher than that calculated from the data by the resonance-antiresonance method. The reason for the difference between the two d_{33} values remains unknown.

Figure 6 shows the temperature dependence of the dielectric constant ϵ and $\tan \delta$ for CBT, CNBT and CN□BT ceramics. The Curie temperature of CBT is 784°C, which is similar to Korzanova's result ($T_c = 790^\circ\text{C}$).¹²⁾ The Curie temperature of CNBT is lower than that of CBT, indicating that A-site sub-

Table I. Lattice parameters of CBT, CNBT and CN□BT.

	a (Å)	b (Å)	c (Å)	V (Å ³)
CBT	5.4329(5)	5.4152(5)	40.78(1)	1199.73
CNBT	5.4269(8)	5.4136(24)	40.71(1)	1195.94
CN□BT	5.4282(12)	5.4137(14)	40.75(2)	1197.51

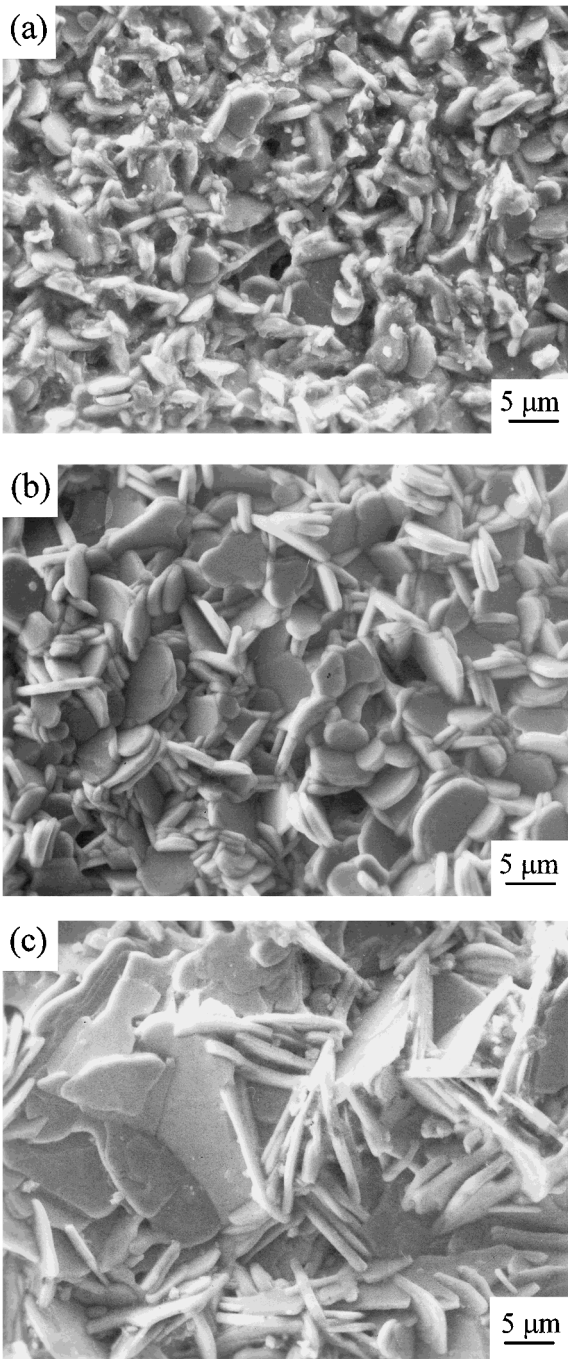


Fig. 3. SEM micrographs of the natural surface of CN□BT fired at (a) 1150°C, (b) 1200°C, and (c) 1250°C.

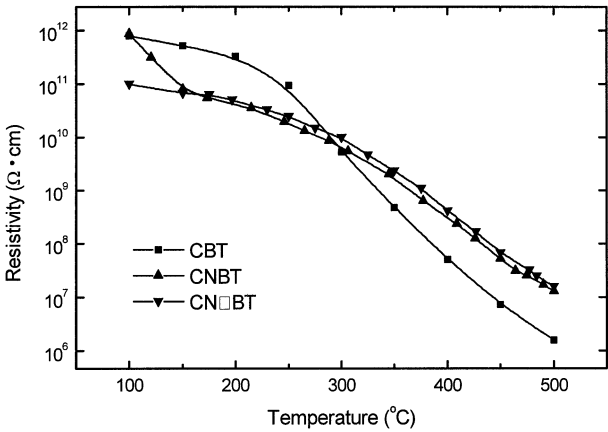


Fig. 4. Temperature dependence of the resistivity ρ of the three materials.

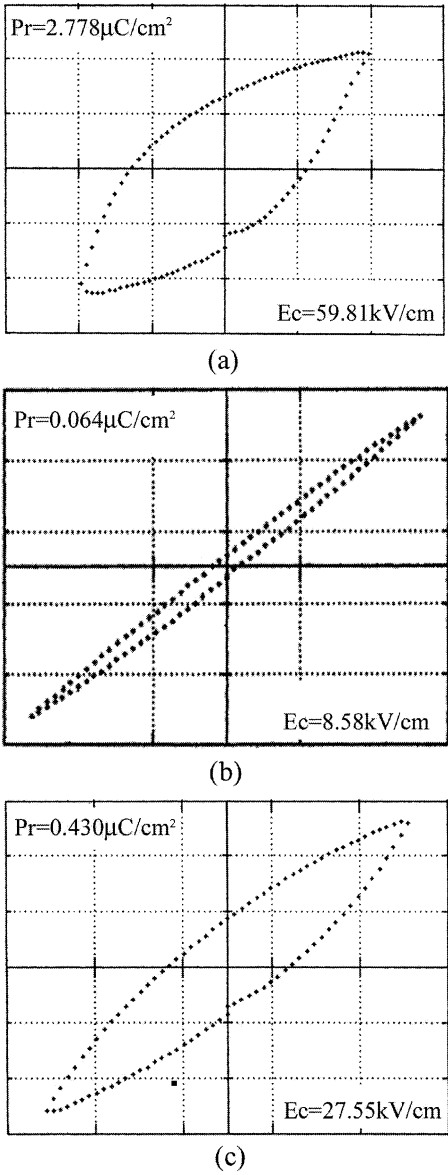


Fig. 5. Hysteresis loops of (a) CBT, (b) CNBT, and (c) CN□BT.

Table II. Piezoelectric and dielectric properties of CBT, CNBT and CN□BT.

	CBT	CNBT	CN□BT
$\epsilon_{33}^T/\epsilon_0$	141	137	140
$\tan \delta$ (%)	0.20	0.11	0.16
d_{33} (pC/N)			
(d_{33} meter)	7	17	20
S_{33}^E (pm ² /N)	8.66	8.64	8.65
k_{33} (%)	3.6	7.2	8.4
d_{33} (pC/N)			
(resonance-antiresonance method)	3.7	7.4	8.7

stitution decreases the Curie temperature of BLSF.¹⁾ However the Curie temperature of Na-deficient CN□BT is 866°C. A similar result was also observed by Shimakawa *et al.*¹³⁾ They systematically investigated the crystal structures and ferroelectric properties of SrBi₂Ta₂O₉ and Sr_{0.8}Bi_{2.2}Ta₂O₉. The structural refinement of Sr_{0.8}Bi_{2.2}Ta₂O₉ revealed that

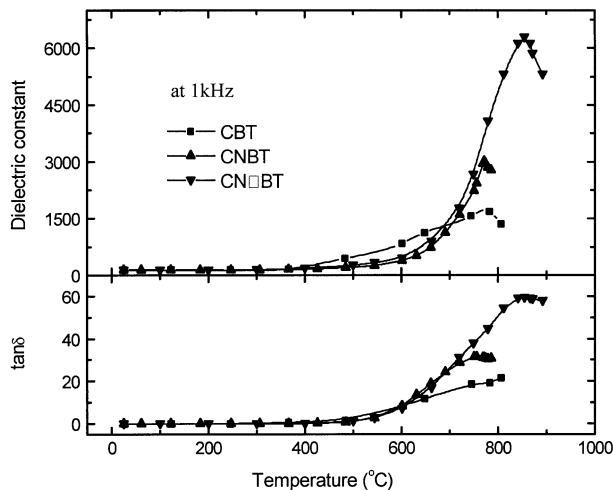


Fig. 6. Temperature dependence of dielectric constant ε and $\tan \delta$ of the three ceramics.

cation vacancies as well as Bi substitution exist at the Sr site. The occupant of the Sr site is $(\text{Sr}_{0.82}\text{Bi}_{0.12}\square_{0.06})$, where \square represents vacancies. The temperature dependence of dielectric constant ε for $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$ samples shows that T_c for the stoichiometric material is 300°C , while that for the Sr-deficient-and-Bi-excess compound increases to 400°C .

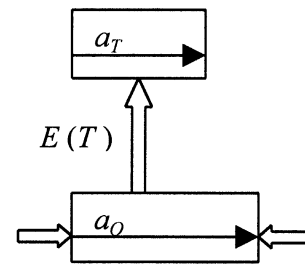
The spontaneous polarization direction of BLSF is along the a -axis.¹⁴⁾ At the Curie point, the orthorhombic ferroelectric phase transforms to the high-temperature paraelectric tetragonal form. The relationship between the axes of the high-temperature tetragonal modification (a_T) and those of the ferroelectric, orthorhombic form (a_o and b_o) is $a_o \cong b_o \cong a_T \times 2^{1/2}$.¹⁵⁾ Thus the phase transition which is related to the change of the a -axis is affected by the internal stress in unit cells.¹⁶⁾ Figure 7 shows the schematic drawing of the effects of stress on the ferroelectric-paraelectric phase transition. ΔE is the phase transition energy, $E(T)$ the heat energy which is a positive function of temperature, and $E(S)$ the stress energy which is a function of stress. The relationship of ΔE , $E(T)$, and $E(S)$ can be expressed as follows.

$$\Delta E = E(T) + E(S) \quad (1)$$

The measurement of T_c was carried out with increasing temperature. Because a_o is larger than a_T , the compressive stress along a -axis promotes the shrinkage of the a -axis, which facilitates the ferroelectric-paraelectric phase transition. Thus, if the stress along a -axis is compressive, then $E(S) > 0$; on the other hand, if the stress along a -axis is tensile stress which obstructs the shrinkage of a -axis, then $E(S) < 0$. From eq. (1), if $E(S) > 0$, then $E(T) < \Delta E$. $E(T)$ in the phase transition decreases, which causes the Curie temperature to decrease because $E(T)$ is a positive function of temperature. If $E(S) < 0$, then $E(T) > \Delta E$. $E(T)$ in phase transition increases, which causes the Curie temperature to increase. The above discussion of stress and Curie temperature can be summarized as follows. If the stress along the a -axis is compressive, the Curie temperature shifts to a lower temperature. On the other hand, if the stress along the a -axis is tensile, the Curie temperature increases, and the grain transforms at a higher temperature. Because it is perovskite-type compound, the shift of the Curie tempera-

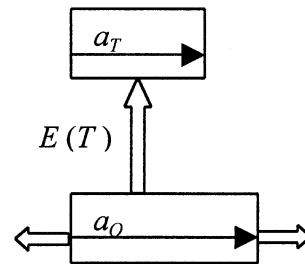
Ferroelectric phase \rightarrow Paraelectric phase

$$\Delta E = E(T) + E(S)$$



Compressive stress, $E(S) > 0$

(a)



Tensile stress, $E(S) < 0$

(b)

Fig. 7. Schematic drawing of effects of stress on the ferroelectric-paraelectric phase transition.

ture of BLSF is also related to the internal stress in unit cells. Compared with CNBT, the expansion of unit cell volume V of $\text{CN}\square\text{BT}$ arises from tensile stress. In $\text{CN}\square\text{BT}$, the lattice parameters a and c are larger (by 0.024% and 0.098%, respectively) while b is slightly larger (by 0.0018%) than those in the CNBT, and thus, tensile stress mainly occurs in the a - c plane. The tensile stress along the spontaneous polarization a -axis makes the ferroelectric-paraelectric phase transition difficult, which may result in the increase of the Curie temperature.

4. Conclusions

The BLSF CBT was modified by A-site (NaCe) substitution with Na-deficiency. The results are summarized as follows:

- (1) The structures of CNBT and $\text{CN}\square\text{BT}$ are a single phase of BLSF with $m = 4$, as revealed by X-ray powder diffraction patterns.
- (2) A-site (NaCe) substitution of CBT results in obvious improvement of the piezoelectric activity and high-temperature resistivity with decreasing Curie temperature.
- (3) A-site (NaCe) substitution with Na-deficiency of CBT not only improves the piezoelectric activity and high-temperature resistivity but also causes a very high Curie temperature.
- (4) Na-deficient $\text{CN}\square\text{BT}$ is an excellent high-temperature piezoelectric material.

- 1) J. P. Mercurio, A. Souirti, M. Manier and B. Frit: *Mater. Res. Bull.* **27** (1992) 123.
- 2) T. Takenaka and K. Sakata: *J. Appl. Phys.* **55** (1984) 1092.
- 3) H. S. Shalman, M. Testorf, D. Damjanovic and N. Setter: *J. Am. Ceram. Soc.* **79** (1996) 3124.
- 4) C. A-Paz de Araujo, J. D. Cuchiaro, L. D. McMillan and M. C. Scott: *Nature* **374** (1995) 627.
- 5) B. Frit and J. P. Mercurio: *J. Alloys & Compd.* **188** (1992) 27.
- 6) L. V. Korzunova and L. A. Shebanov: *Ferroelectrics* **93** (1989) 111.
- 7) K. E. Jonhannson, T. Palm and P.-E. Werner: *J. Phys. E* **13** (1980) 1289.
- 8) P.-E. Werner: *Ark. Kem.* **31** (1969) 513.
- 9) E. C. Subbarao: *J. Am. Ceram. Soc.* **45** (1962) 166.
- 10) M. Villegas, A. C. Caballero, C. Moure, P. Durán and J. F. Fernández: *J. Am. Ceram. Soc.* **82** (1999) 2411.
- 11) K. Shoji, M. Aikawa, Y. Uehara and K. Sakata: *Jpn. J. Appl. Phys.* **37** (1998) 5273.
- 12) L. Korzanova: *Ferroelectrics* **134** (1992) 175.
- 13) Y. Shimakawa, Y. Kubo, Y. Nakagawa, T. Kamiyama, H. Asano and F. Izumi: *Appl. Phys. Lett.* **74** (1999) 1904.
- 14) R. L. Withers, J. G. Thompson and A. D. Rae: *J. Solid State Chem.* **94** (1991) 404.
- 15) E. C. Subbarao: *J. Phys. & Chem. Solids* **23** (1962) 665.
- 16) H. J. Hwang, T. Nagai, T. Ohji, M. Sando, M. Toriyama and K. Niihara: *J. Am. Ceram. Soc.* **81** (1998) 709.