

# Effect of poling conditions on growth of calcium phosphate crystal in ferroelectric BaTiO<sub>3</sub> ceramics

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Recently, ceramic materials have been given a lot of attention as candidates for implant materials, since they possess biologically favorable characteristics for osseointegration. Among them, BaTiO<sub>3</sub> (BTO) ceramics are ferroelectric and piezoelectric after poling treatments. However, little or no information is available on the poling condition of BTO and their effect on calcium phosphate (CaP) formation. In this study, the effect of poling conditions on the formation of CaP layer was investigated. It was observed from this study that CaP was formed on negatively charged BTO surfaces. An increase in Ca/P ratio to 1.67 was observed when the poling temperature was increased above the Curie temperature. On positively charged BTO, no CaP layer was observed.

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## 1. Introduction

The knowledge that ferroelectric barium titanate (BaTiO<sub>3</sub>, BTO) possesses high permittivity ( $\epsilon_r$ ) have allowed their use in the manufacture of ceramic capacitors in 1943 [1, 2]. When BTO cools through its Curie temperature ( $T_c$ ), the initially cubic material becomes tetragonal by elongating along a cube axis while the other two cube axes contract (Fig. 1). Extreme dielectric anomalies accompany this transition which signals the onset of ferroelectricity and the replacement of the centro-symmetric cubic structure by a polar one. Upon further cooling, other transitions occur at 5 °C and –90 °C. As shown in Fig. 1, these structures are pseudomonoclinic, but are actually orthorhombic and rhombohedral, respectively [3].

As a result of BTO's high dielectric constant and ferroelectric properties at temperatures below 120 °C ( $T_c$ ) where it assumes a tetragonal phase, BTO can be found in a wide range of applications in electronic and electro-optic devices [4–8]. Moreover, BTO with a textured surface have been used as medical implants in experimental trials to improve osseointegration [9]. This material becomes ferroelectric by poling treatment, which has been suggested to easily attract cation such as Ca<sup>2+</sup> on its negatively charged surface. The attracted cation would be assumed to behave as nuclei for bone-like crystal growth in human plasma. K. Yamashita [10] has reported the phenomenological effects of polariza-

tion on the acceleration and deceleration of bone-like crystal growth on hydroxyapatite (HAP) ceramics, calcium titanate and BTO. However, there is limited information available on the effect of poling condition on bone-like crystal growth on ferroelectric BTO ceramics. Thus, in this study, the formation of calcium phosphate (CaP) after immersing poled BTO substrates in simulated body fluid (SBF) was investigated.

## 2. Materials and methods

### 2.1. Material preparation

A commercial-grade BTO raw material (Aldrich Co, Milwaukee, WI) with Ba/Ti = 1.00 and average particle size of  $\leq 1 \mu\text{m}$  was used. Fig. 2 shows the experimental procedure. The raw material was initially weighed followed by wet ball milling for 24 h to eliminate aggregates and/or reduce the particle size. Zirconia balls were used in a Teflon bottle and the liquid used was methanol. The ratio of liquid to powder used was 2 : 1 by volume. The milled sample was dried at 100 °C for 24 h and preformed into disks. The preformed disks were cold isostatically pressed (CIP) without binder at 1400 kg/cm<sup>2</sup>. Sintering of the disks was performed in air at 1300 °C for 2 h in a tube furnace, with heating and cooling rates of 5 °C/min and 2–3 °C/min, respectively. Following sintering, the BTO ceramics were polished, with final polishing using 0.3  $\mu\text{m}$  alumina slurry. The

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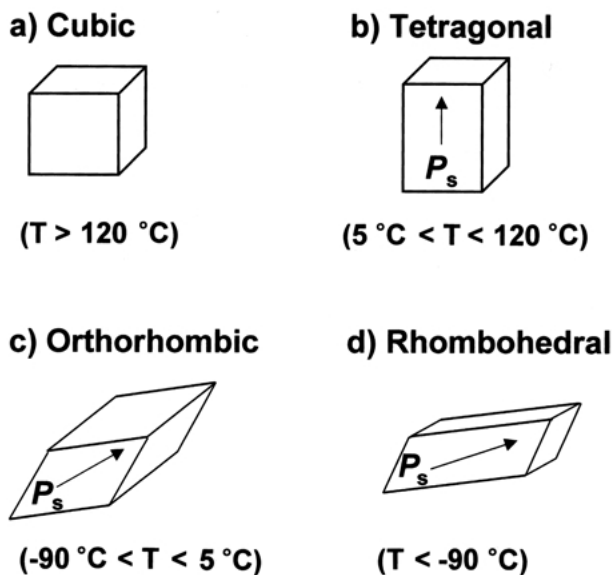


Figure 1 Crystallographic changes of BTO unit cell according to the temperature. variation ( $P_s$ : spontaneous polarization).

samples were then cleaned by distilled water in ultrasonic bath.

## 2.2. Analysis of polished BTO samples

The crystalline structure and the dielectric permittivity of polished BTO samples were evaluated. X-ray diffraction analysis (XRD) (D-Max-1200, Rigaku Co.) utilizing  $\text{CuK}\alpha$  radiation was used to measure the crystalline structure. The  $a$ - and  $c$ -lattice spacing of the standard bulk tetragonal BTO and polished BTO sample prepared in this study was calculated using the (1 0 1)/(1 1 0) peak. The standard bulk tetragonal BTO was used as a standard for comparison to the polished BTO sample. The dielectric permittivity of BTO was measured with an Impedance Analyzer (HP 4194A, Hewlett Packard Co.).

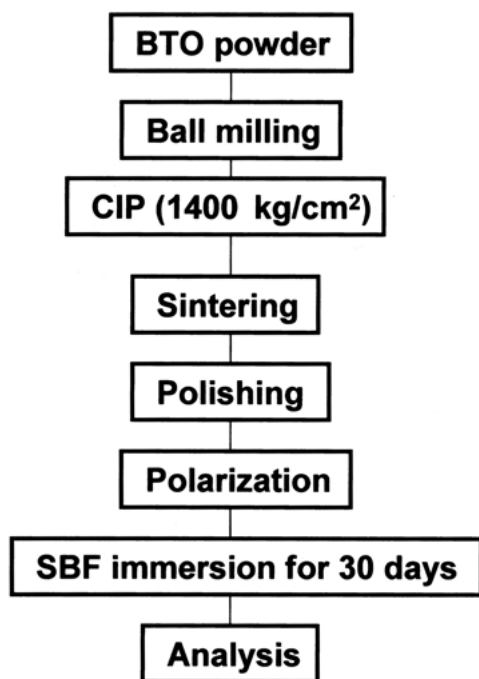


Figure 2 Schematic representation of the procedure used for the sample preparation, poling treatment and analysis.

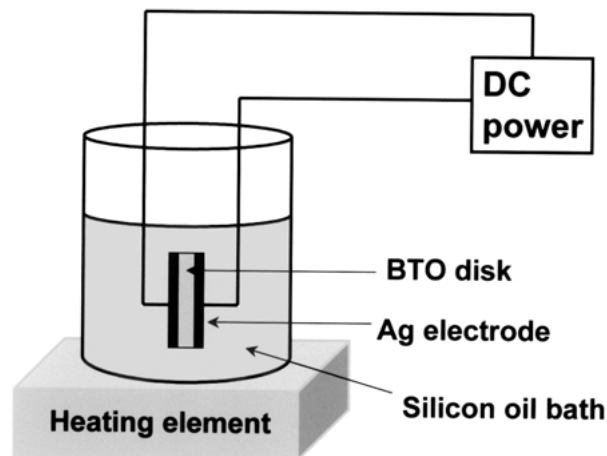


Figure 3 A schematic drawing showing the apparatus used for poling.

## 2.3. Poling treatment

Prior to poling treatment, polished BTO disks were electroded with silver paste, and heat-treated at  $590^\circ\text{C}$  for 10 min to achieve ohmic contact between the BTO disk and the silver electrode. As shown in Fig. 3, poling of BTO was performed by applying a strong electric field to the electroded BTO. The field may be continuous and intermittent, and the charging strength was varied depending on the thickness and shape of the samples. Because of the low dielectric strength of air, silicon oil bath was used. In this study, the following three poling conditions used were (1) room temperature poling treatment [polarizing field ( $E_p$ ) = 25 kV/cm at  $25^\circ\text{C}$  for 2 h, (2) middle temperature poling treatment below  $T_c$  ( $E_p = 20$  kV/cm) from  $85^\circ\text{C}$  to  $25^\circ\text{C}$  for 2 h, (3) high temperature poling treatment above  $T_c$  ( $E_p = 5$  kV/cm) from  $160^\circ\text{C}$  to  $25^\circ\text{C}$  for 2 h. These three conditions were used to investigate the effect of poling condition, particularly poling temperature, on the formation of bone-like crystals *in vitro*.

## 2.4. Immersion test

The *in vitro* formation of CaP was evaluated by immersing the poled BTO samples in SBF. The SBF was prepared by dissolving NaCl,  $\text{NaHCO}_3$ , KCl,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_4$  in deionized distilled water. To this solution, 50 mM tris-(hydroxymethyl) aminomethane [ $(\text{CH}_2\text{OCH}_3)_3\text{CNH}_2$ ] and 45 mM hydrochloric acid (HCl) were used as buffering agents to maintain the pH of SBF at 7.25 at  $36.5^\circ\text{C}$ . These buffering agents have been reported to perform the buffering function in the body fluid [11]. The reagent-grade chemicals used and its concentrations for the preparation of SBF are shown in Table I.

Duplicate samples/poled condition were immersed in 15 mL of SBF for 30 days. The experiment was performed in a constant temperature-circulating bath (Model 90, Poly Science Co.) at a temperature of  $36.5^\circ\text{C}$ . After soaking, the samples were removed from the SBF, carefully rinsed with distilled water, and dried at room temperature.

TABLE I Reagents for preparing the simulated body fluid

Adding order	Reagent	Amount g/L H <sub>2</sub> O
1	(CH <sub>2</sub> OH) <sub>3</sub> CNH <sub>2</sub>	6.055
2	NaCl	7.995
3	NaHCO <sub>3</sub>	0.353
4	KCl	0.224
5	K <sub>2</sub> HPO <sub>4</sub> · 3H <sub>2</sub> O	0.228
6	MgCl <sub>2</sub> · 6H <sub>2</sub> O	0.305
7	CaCl <sub>2</sub> · 2H <sub>2</sub> O	0.368
8	Na <sub>2</sub> SO <sub>4</sub>	0.071
9	2 mol/L HCl	20 mL

### 2.5. Analysis of poled BTO samples after immersion

The morphology and composition of the surface of the soaked samples were evaluated using field emission scanning electron microscope (FE-SEM) (S-4700, Hitachi Co.) equipped with an energy dispersive X-ray spectrometer (EDX) that has a Robinson type back-scattered electron detector.

### 3. Results

As shown in Fig. 4, a typical XRD pattern indicated that the BTO disk crystallized after sintering at 1300 °C for 2 h. Peaks corresponding to the perovskite BTO alone were observed, whereas no peaks from metastable pyrochlore phases were present. Using the (002) and (200)/(020) peaks, the *a*- and *c*-lattice spacings of BTO disks were observed to be 0.399(2) and 0.402(9) nm, respectively. The ratio of *c* spacing : *a* spacing was 1.009.

Fig. 5 shows a SEM micrograph of polished and acidic etched surface of BTO sample. It was observed from the SEM micrograph that the average grain size of the BTO microstructure after at sintering temperature of 1300 °C was ≤ 1 μm. In addition, the relative dielectric constant of BTO at 1 kHz (at room temperature) was observed to be 3000 ~ 3500.

Figs 6–8 show the ionic concentrations and SEM micrographs of the negatively charged BTO (N-BTO) surfaces after immersing the poled samples in SBF for 30 days, and Fig. 9 shows those of the positively charged BTO (P-BTO) surface. Morphological analysis of the N-BTO samples using SEM shows a rough, heterogeneous and melt-like surface. EDX analysis of the N-BTO surfaces indicated the presence of calcium (Ca) and

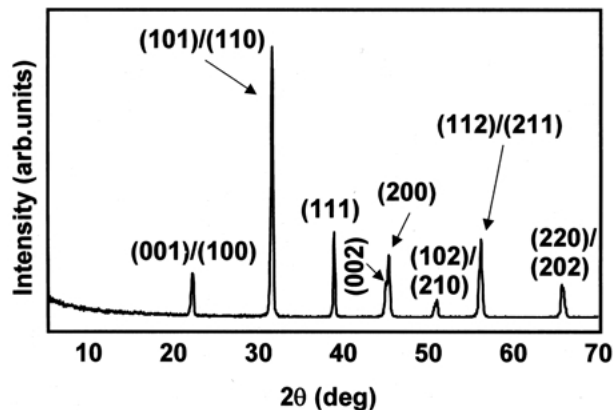


Figure 4 XRD pattern of BTO sintered at 1300 °C for 2 h.

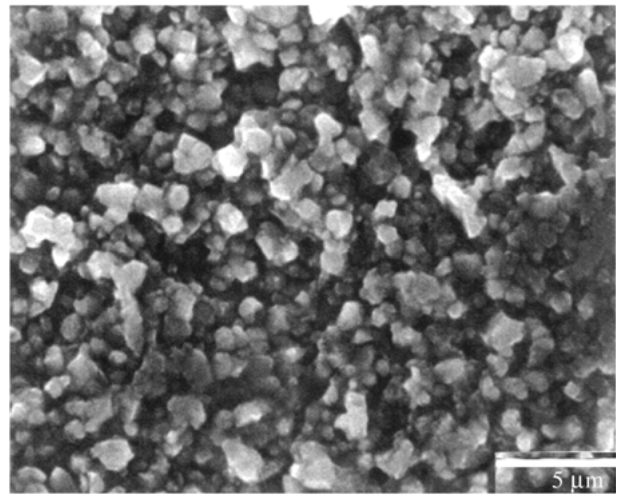


Figure 5 SEM photograph of BTO sintered at 1300 °C for 2 h.

phosphorus (P) on all poled N-BTO samples after immersion. However, the ability of the N-BTO samples to form a calcium phosphate (CaP) layer on the surfaces after immersion in SBF was observed to vary with poling conditions, with an increased concentration of Ca and P as the poling temperature becomes higher. The Ca/P ratio of N-BTO poled at temperature below *T<sub>c</sub>* was observed to be in the range 1.2–1.5, whereas N-BTO disks poled at temperature above *T<sub>c</sub>* was observed to be in the range 1.5–1.67.

SEM micrographs of the positively charged BTO (P-BTO) surface indicated significant morphological changes after 30 days immersion in SBF. However, no Ca and P formation was observed on the P-BTO surface.

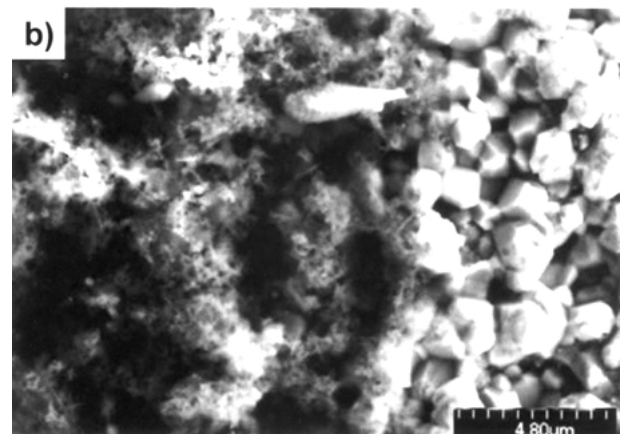
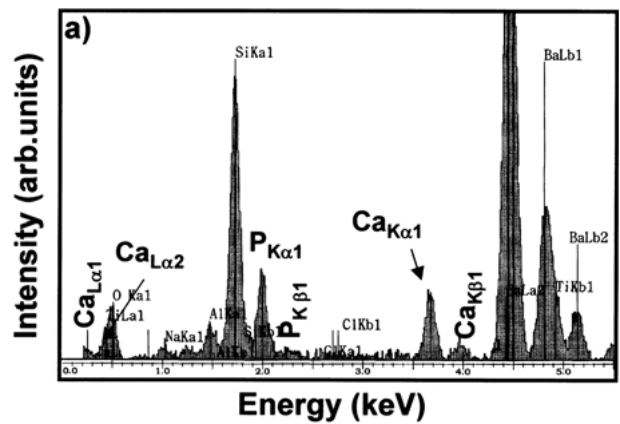


Figure 6 EDX spectrum and surface morphology of N-BTO poled by condition 1 and immersed in SBF for 30 days.

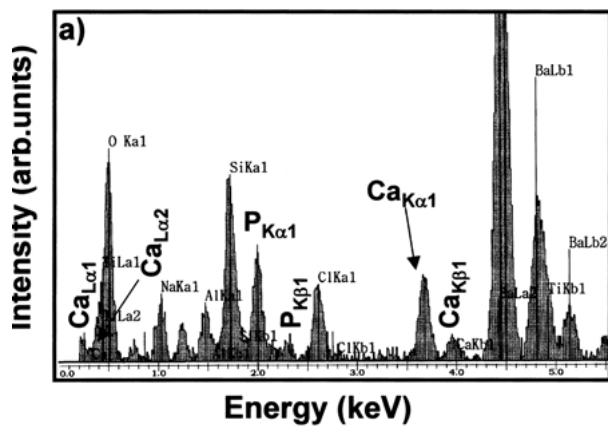


Figure 7 EDX spectrum and surface morphology of N-BTO poled by condition 2 and immersed in SBF for 30 days.

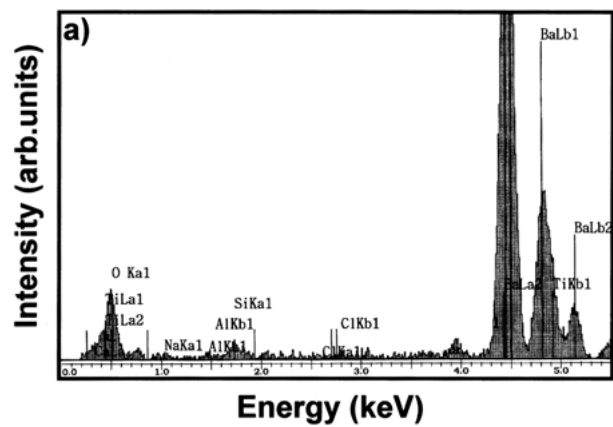


Figure 9 EDX spectrum and surface morphology of P-BTO poled by condition 3 and immersed in SBF for 30 days.

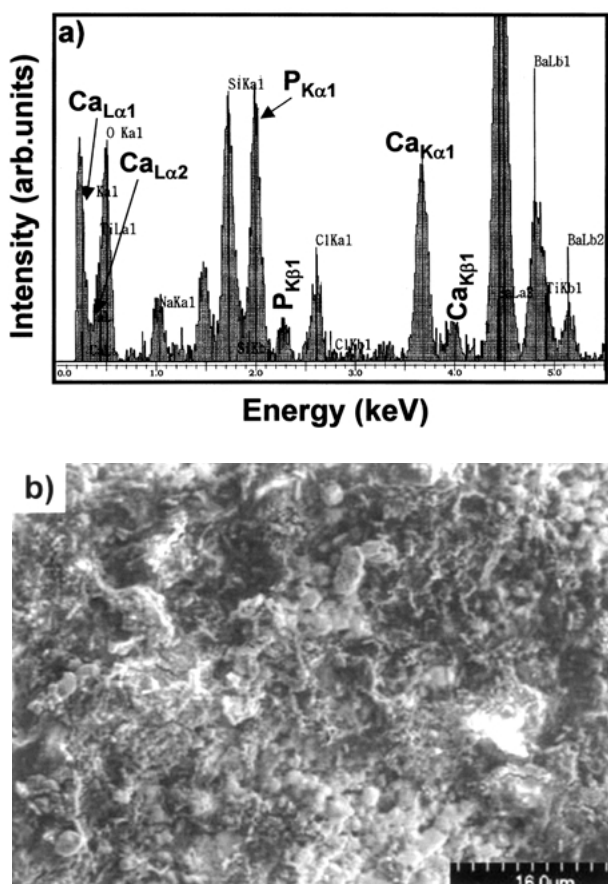


Figure 8 EDX spectrum and surface morphology of N-BTO poled by condition 3 and immersed in SBF for 30 days.

#### 4. Discussion

One of most valuable features of ferroelectric behavior is that ferroelectric ceramics such as BTO and  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT), can be transformed into polar materials by applying a static electrical field. However, heavy metal such as Pb in PZT can be definitely classified into harmful ion for human body although the mechanism is not clearly understood in biomaterials [12]. Thus, among ferroelectric materials, BTO is chosen in the present work since there is no information on its toxicity for the human body. As shown in this study, crystallized BTO was observed after sintering at  $1300^\circ\text{C}$  for 2h, with peaks corresponding to perovskite BTO. As reported in other studies, peaks from the metastable pyrochlore phases were not observed after sintering [13]. Other studies have indicated that the tetragonal phase of the BTO disks was best identified by the splitting of the peak with  $2\theta$  around  $45 \sim 46^\circ$  into two peaks, which correspond to the (002) and the (200)/(020) reflections [14]. In addition, the  $c/a$  ratio of the BTO disks was 1.009, which was similar to that of the standard bulk tetragonal BTO ( $c_0/a_0 = 0.4038/0.3994 = 1.0110$ ) [13]. In addition, other studies have reported similar relative dielectric constant of BTO at 1 kHz at room temperature [15, 16].

It is also known that the Curie point of pure crystal and polycrystalline BTO is  $120^\circ\text{C}$ . When the BTO is poling through the Curie point, a particular domain pattern is formed and the physical imperfections are easily aligned as a result of the stresses created. This formation of a particular domain pattern is also compensated by

changes in surface charges. As a result of structural reformation, variation in the ferroelectric and dielectric properties of the BTO was suggested to occur. However, the BTO undergoes partial upset of its twins with eliminating much of the domain structure after poling treatment since the practical dipole orientation in the BTO does not reach the fully oriented value for several reasons such as intergranular stresses and imperfections causing strains within the grains.

In this study, three poling conditions were investigated. As observed in this study, the N-BTO surfaces at all poling conditions exhibited a rough, heterogeneous and melt-like morphology. Chemical analysis of these surfaces after immersion in SBF indicated a lower Ca/P ratio (1.2–1.5) for N-BTO samples poled at temperature below  $T_c$ , whereas a higher Ca/P ratio (1.5–1.67) was observed for N-BTO samples poled at temperature above  $T_c$ . This Ca/P ratio suggested that the N-BTO surface was similar to the biological calcium phosphate (CP) [17, 18] after poling at temperature above  $T_c$ . Since the dipoles are most easily aligned during cooling down through the  $T_c$  [19], our study indicates that poling above  $T_c$  is very effective for the formation of CaP on N-BTO surface.

On positively charged BTO (P-BTO) surfaces, no CaP formation was observed. In order to explain the differences in CaP formation on N-BTO and P-BTO surfaces, a plausible mechanism for CaP formation on N-BTO after immersion in SBF was illustrated in Fig. 10. After poling treatment, cation such as  $\text{Ca}^{+2}$  dissolved in SBF was suggested to be rapidly adsorbed on N-BTO surface, whereas no  $\text{Ca}^{+2}$  ions was adsorbed on the P-BTO surface. Anions such as  $\text{HPO}_4^{-2}$  and  $\text{OH}^-$  dissolved in SBF were then suggested to form around the previously adsorbed cations. Thus,  $\text{Ca}^{+2}$  ions on the N-BTO surface acted as nuclei for the formation of CaP, while no nuclei was present on P-BTO surface for CaP formation.

The phenomena of CaP formation on metallic surface has been reported in the literature [20, 21]. However, this study on BTO ceramic surfaces corresponded to the clinical reports and provides evidences that bone could be formed more easily around negative-charged surfaces [22, 23]. The effect of electrical stimulation on bone formation have been widely studied since Yasuda reported that bone could be formed around the electrode during continuous stimulation of an electrical micro-current for several weeks [24–27]. Furthermore, many authors have demonstrated the ability of small amounts of electric current to stimulate bone formation in the region of a cathode. At present, the electrical stimulation methods such as constant direct current stimulation [28, 29], pulsed direct current [30], pulsing electromagnetic field [31] and various forms of inductive coupling [32–34] have been adapted for orthopedic applications. It was suggested that cathodic stimulation stimulated bone formation in an area where bone formation was not in process [22]. A direct constant-current cathode was suggested to cause bone formation at a site remote from any bone trauma in the medullary cavity of a rabbit tibia. Thus, as suggested by reports on the effect of electrical stimulation on bone formation, the N-BTO behaves like a cathode, thereby accelerating CaP formation. Further studies are needed to test this hypothesis and to evaluate the use the ferroelectric property of BTO for the improvement of bone formation around implants.

## 5. Conclusions

N-BTO ceramics poled at various conditions formed a CaP layer after immersion in SBF. However, the Ca/P ratio of the CaP formed on N-BTO discs is dependent on the poling condition, with Ca/P ratio approaching 1.67 after poling the BTO discs above  $T_c$ . No CaP formation was observed on P-BTO discs. It was concluded from this

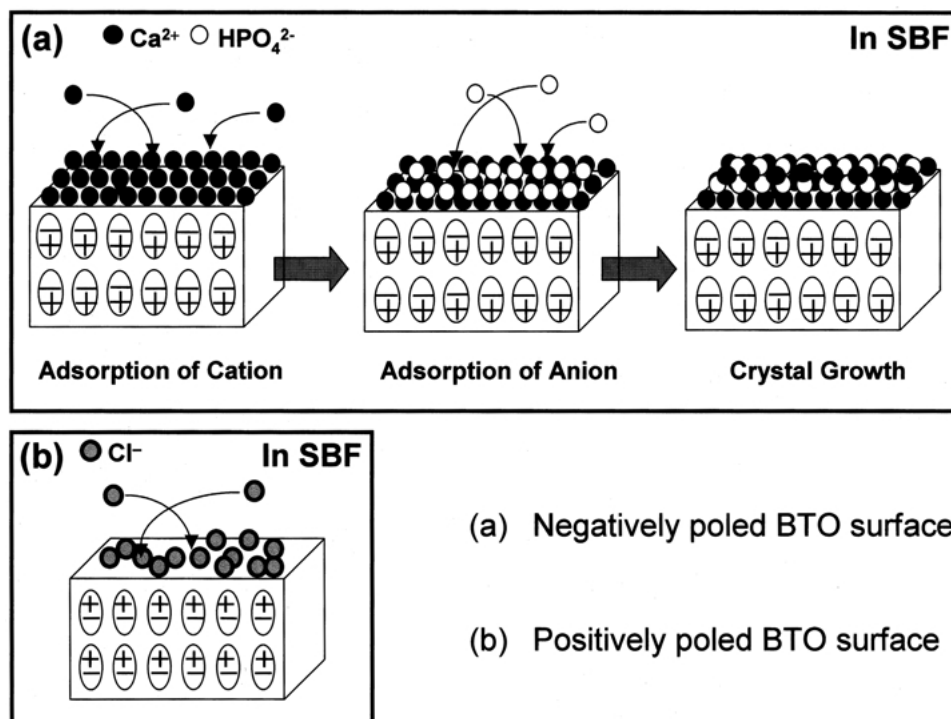


Figure 10 Schematic illustrations of possible mechanism for CaP formation.

study that a negatively-charge surface is required for CaP formation.

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## References

1. L. SHEPPARD, *Am. Ceram. Soc. Bull.* **72** (1993) 45.
2. J. M. WILSON, *ibid.* **74** (1995) 106.
3. B. JAFFE, W. R. COOK, JR and H. JAFFE, in "Piezoelectric Ceramics" (Academic Press, London and New York, 1971) p. 53.
4. A. J. MOULSON and J. M. HERBERT, in "Electroceramics" (Chapman and Hall, London, 1990) p. 68.
5. S. TSUNEKAWA, T. FUKUDA, T. OZAKI, Y. YONEDA, T. OKABE and H. TERAUCHI, *J. Appl. Phys.* **84** (1998) 999.
6. G. ARLT, D. HENNINGS and G. DE WIT, *ibid.* **58** (1985) 1619.
7. A. J. BELL, A. J. MOULSON and L. E. CROSS, *Ferroelectrics* **54** (1984) 147.
8. C. L. JIA, K. URBAN, S. HOFFMANN and R. WASER, *J. Mater. Res.* **13** (1998) 2206.
9. J. B. PARK and R. S. LAKES, in "Biomaterials – An Introduction" (Plenum Press, New York and London, 1991) p. 130.
10. K. YAMASHITA, N. OIKAWA and T. UMEGAKI, *Chem. Mater.* **8** (1996) 2697.
11. Y. ABE, T. KOKUBO and T. YAMAMURO, *J. Mater. Sci.: Mater. Med.* **1** (1990) 233.
12. S. BUDAVARI, M. J. O'NEIL, A. SMITH and P. E. HECKELMAN, in "The Merck Index" (Merck & Co., Inc., Rahway, 1989) p. 851.
13. 1997 JCPDS-International Centre for Diffraction Data (JCPDS File 05-0626).
14. T. HAYASHI, N. OJI and H. MAIWA, *Jpn. J. Appl. Phys.* **33** (1994) 5277.
15. W. R. BUESSEM, L. E. CROSS and A. K. GOSWAMI, *J. Am. Ceram. Soc.* **49** (1996) 36.
16. Y. MA, E. VILENO, S. L. SUIB and P. K. DUTTA, *Chem. Mater.* **9** (1997) 3023.
17. T. IKOMA, A. YAMAZAKI, S. NAKAMURA and M. AKAO, *J. Mater. Sci. Lett.* **18** (1999) 1225.
18. Y. HAN, K. XU and J. LU, *J. Mater. Sci.: Mater. Med.* **10** (1999) 243.
19. B. JAFFE, W. R. COOK, JR and H. JAFFE, in "Piezoelectric Ceramics" (Academic Press, London and New York, 1971) p. 75.
20. J. L. ONG, G. N. RAIKAR, L. C. LUCAS, R. CONNATSER and J. C. GREGORY, *J. Mater. Sci.: Mater. Med.* **6** (1995) 113.
21. D. KAWAHARA, J. L. ONG, G. N. RAIKAR, L. C. LUCAS, J. E. LEMONS and M. NAKAMURA, *International J. Oral Maxillofac. Implan.* **11** (1996) 435.
22. J. A. SPADARO, *Bioelectromagnetics* **18** (1997) 193.
23. C. ANDREW, L. BASSETT, R. J. PAWLUK and R. O. BECKER, *Nature* **204** (1964) 652.
24. N. N. SALMAN and J. B. PARK, *Biomater.* **1** (1980) 209.
25. Z. B. FRIEDENBERG, L. M. ZEMSKY, R. P. POLLIS and C. T. BRIGHTON, *J. Bone Joint Surg.* **56-A** (1974) 1023.
26. L. S. LAVINE, I. LUSTRIN and M. H. SHAMOS, *Nature* **224** (1969) 1112.
27. I. YASUDA, K. NOGUCHI and T. SATA, *J. Bone Joint Surg. Am.* **37** (1955) 1292.
28. L. S. LAVINE, I. LUSTRIN, M. H. SHAMOS, R. A. RINALDI and A. R. LIBOFF, *Science* **175** (1972) 1118.
29. C. MASUREIK and C. ERIKSSON, *Clin. Orthop.* **124** (1977) 84.
30. T. E. JØRGENSEN, *ibid.* **124** (1977) 124.
31. T. SHIMIZU, J. E. ZERWEKH, T. VIDEMAN, K. GILL, V. MOONEY, R. E. HOLMES and H. K. HAGLER, *J. Orthopaed. Res.* **6** (1988) 248.
32. C. A. L. BASSETT, R. J. PAWLUK and A. A. PILLA, *Science* **184** (1974) 575.
33. C. A. L. BASSETT, A. A. PILLA and R. J. PAWLUK, *Clin. Orthop.* **124** (1977) 128.
34. C. A. L. BASSETT, S. N. MITCHELL, L. NORTON and A. A. PILLA, *Acta. Orthop. Belg.* **44** (1978) 706.

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