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STUDY OF BISMUTH LAYER-STRUCTURED FERROELECTRICS FOR HIGH-TEMPERATURE APPLICATIONS

SUBMITTED BY
HU TIAN TIAN

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF PHILOSOPHY IN APPLIED PHYSICS

AT
THE DEPARTMENT OF APPLIED PHYSICS
THE HONG KONG POLYTECHNIC UNIVERSITY

September, 2005
CERTIFICATE OF ORIGINALITY

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_________________________(Signed)

HUITIANTIAN (Name of student)
Abstract

With the trends in environmental protection, there are growing interest and demand in developing lead-free ferroelectric materials for replacing the currently used lead-based materials in various piezoelectric and pyroelectric applications. In the present work, bismuth titanate-based ferroelectric materials Bi$_{3.5-x}$Nd$_{0.5}$Ti$_{3-x}$Nb$_x$O$_{12}$ (BNTN), both in the forms of ceramic and film, with good piezoelectric and pyroelectric properties have been successfully fabricated and have been shown to be potential candidates for high-temperature sensor applications.

BNTN ceramics were prepared using a conventional mixed-oxide technique. The ceramics were sintered well into a single phase of bismuth layered perovskite structure at 1000°C for 4 hours. The effects of the niobium (Nb) dopant on the electrical, ferroelectric, piezoelectric and pyroelectric properties have then been investigated and discussed. No significant effect of the Nb dopant on the Curie temperatures (T$_c$) is observed; all the BNTN ceramics exhibit similar high values of T$_c$ (~ 540°C). Concluding from the observations on the temperature and frequency dependences of the dielectric loss, the Nb dopant can effectively reduce the oxygen vacancies in the BNTN ceramics, while the oxygen vacancies are responsible for the high conductivity of the bismuth titanate-based ceramics. Our results also reveal that after the doping with Nb, the dielectric constant $\varepsilon$, coercive field $E_c$ and leakage current $J$ of the Bi$_{3.5}$Nd$_{0.5}$Ti$_3$O$_{12}$ (BNT) ceramic decrease, while its remanent polarization $P_r$, piezoelectric (charge) coefficient $d_{33}$ and pyroelectric coefficient $p$ increase. At the optimum doping level (~ 6 mol%), the ceramic exhibits the largest
Abstract

P_y (15 µC/cm^2), largest d_{33} (22 µC/N), largest p (129 µC/m^2K), and the lowest J (3×10^{-8} A/cm^2). Since the ceramics also have a relatively low value of ε (~ 99), their piezoelectric (voltage) coefficient and figure of merit for pyroelectricity are large and comparable to those of a lead-based ferroelectric ceramic. Together with the high Curie temperature, the BNTN ceramics therefore should be good candidates for various high-temperature sensing applications.

For MEMS application studies, Bi_{3.5}Nd_{0.5}Ti_3O_{12} (BNT) thin films of thickness 900 nm have been successfully fabricated on platinized silicon substrates using a sol-gel method. The dielectric, ferroelectric as well as the piezoelectric and pyroelectric properties of the films were investigated. Our results reveal that the BNT thin films can crystallize well into a single phase of bismuth layered perovskite structure at 650°C and 700°C. However, a higher annealing temperature results in larger grains and better properties. For the BNT thin film annealed at 700°C, the observed ε, tanδ, P, p and e_{31,f} are 132, 0.034, 22 µC/cm^2, 148 µC/m^2K and 1.45 C/m^2, respectively. Similar to the cases for ceramics, owing to the low ε, the piezoelectric (voltage) coefficient and figure of merit for pyroelectricity of the films are large and comparable to those of a lead-based ferroelectric thin film. Therefore, the BNT thin films could be employed in various sensor applications.
Acknowledgments

Without the great help of many kind people, this work would not have been possible.

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Last, but not least, I appreciate the financial support from the Hong Kong Polytechnic University and the technical support provided by the Centre of Smart Materials of the Hong Kong Polytechnic University.
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Chapter One

Introduction

1.1 Background

After 1880 when the piezoelectric effect was discovered by Pierre Curie and Jacques Curie [Jaffe, 1971], the importance of piezoelectric materials has risen up in society. During the past 30 years, piezoelectric materials have been studied intensively and widely. Among all the piezoelectric candidates, lead-based materials, such as lead zirconate titanate (PZT), exhibit excellent piezoelectric properties as well as good ferroelectric and pyroelectric properties. For the prominent performance in non-volatile memory applications and new micro-electromechanical systems (MEMS), such as sensors, actuators and transducers, lead-based piezoelectric materials have attracted considerable attention in electronic industry.

However, due to environmental concerns, there is a tendency to restrict the use of lead-containing devices. As far as people known, lead can affect almost every organ and system in human bodies, especially the central nervous system, kidneys and the reproductive system. At high dosages, lead may decrease reaction time, cause weakness in fingers, wrists or ankles, and possibly affect the memory. It may also cause anemia and the disorder of the blood.
Although in the marine environment, high concentrations of lead can be accumulated with no apparent harm, lead itself does not break down. When lead is released to air, it may travel long distances before settling to the ground. Once lead falls onto soil, it usually sticks to soil particles, and then can be taken into the water cycling system of the earth by rains. After resolving, lead that used in industrial products, especially in electronic devices, will be put into the groundwater, and finally absorbed into organisms. In addition, lead-based materials are incompatible with biological systems; thus, for piezoelectric devices which are to be implanted into biological systems, e.g. human body, there is a need to develop piezoelectric materials that are free of lead or have reduced content of lead.

Under these circumstances, lead-free piezoelectric materials have attracted considerable attentions in recent years. Research work was expanded from the studies on barium titanate (BaTiO₃), of which many patents have been developed in the first several years. With the development of the study in lead-free materials, more and more different lead-free piezoelectric systems were investigated. Based on the latest studies, there are four main systems that have drawn most interest in electronic fields:

1. Barium titanate (BaTiO₃)-based lead-free piezoelectric system,
2. Bismuth sodium titanate (Bi₁/₂Na₁/₂TiO₃)-based lead-free piezoelectric system,
3. Alkaline niobate-based lead-free piezoelectric system, and
Nowadays, lead-free piezoelectric materials have been widely used in a lot of electronic applications. One can find out the trend and the development of lead-free piezoelectric materials from the change in the number of patents relating to lead-free piezoelectric ceramics in the last 20 years (Table 1.1). It is obvious that the lead-free piezoelectric materials are being widely developed and will take the leading role in the future.

Table 1.1 Distributions of the patents of lead-free piezoelectric ceramic [Lin, 2003].

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<td>6</td>
<td>5</td>
<td>3</td>
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<td>2</td>
<td>1</td>
<td>2</td>
<td>16</td>
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<td>titanate-based</td>
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<td>BLSF</td>
<td>2</td>
<td>13</td>
<td>2</td>
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<td>Sum.</td>
<td>20</td>
<td>28</td>
<td>12</td>
<td>79</td>
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### 1.2 Lead-Free Piezoelectric Systems

#### 1.2.1 Barium Titanate (BaTiO$_3$)-Based System

The study on barium titanate is carried out by far the most intensively and extensively. Barium titanate has a typical perovskite ABO$_3$ structure which is shown in Figure 1.1. In the ABO$_3$ structure, the large cation (A) is on the corners while the small cation (B) in the body centre, and oxygen locates in the centre of the faces. Most of the materials with ABO$_3$ structure have a structural phase transition from a high-temperature non-ferroelectric (or paraelectric) phase into a low-temperature ferroelectric phase that exhibits hysteresis behaviors of polarization under the influence of electric field. The temperature of the transition is defined as Curie temperature, $T_c$ [Lines, 1979]. Figure 1.2 shows the phase transition in BaTiO$_3$.

![Image](image.png)

Figure 1.1 Structure of barium titanate unit cell [Kusumoto, 2005].
Barium titanate is an important candidate for capacitors and has been produced in mass. Pure barium titanate has weak piezoelectric properties and a very low Curie temperature at 120°C which limiting its use in various applications. The stability of this material is also poor and cannot be improved by doping with other elements. However, after replacing part of Ti by Zr and adding metallic oxides, the new system $\text{Ba}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ becomes a good piezoelectric material, having larger piezoelectric coefficients and electromechanical coupling coefficients, and a more stable structure [Yin, 2004].
This piezoelectric system can be divided into three structures:

(1) \((1-x)\text{BaTiO}_3-x\text{ABO}_3\) (A = Ba, Ca, etc.; B = Zr, Sn, etc.)

(2) \((1-x)\text{BaTiO}_3-x\text{A}'\text{B}'\text{O}_3\) (A' = K, Na, etc.; B' = Nb, Ta, etc.)

(3) \((1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{NbO}_3\) (M = Ca, Sr, Ba, etc.)

The properties of some barium titanate-based piezoelectric ceramics are shown in Table 1.2 [Yin, 2004].

<table>
<thead>
<tr>
<th>(x)</th>
<th>(y)</th>
<th>(a)</th>
<th>(\text{CuO} (%))</th>
<th>(\text{ZrO}_2 (%))</th>
<th>(d_{33} (\text{pC/N}))</th>
<th>(k_{33} (%))</th>
<th>(T_c (^{\circ}\text{C}))</th>
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<tr>
<td>1.00</td>
<td>0.01</td>
<td>-</td>
<td>0.20</td>
<td>-</td>
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<td>1.00</td>
<td>0.12</td>
<td>-</td>
<td>0.20</td>
<td>-</td>
<td>352</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>1.00</td>
<td>0.05</td>
<td>0.10</td>
<td>0.20</td>
<td>0.25</td>
<td>-</td>
<td>64</td>
<td>106</td>
</tr>
<tr>
<td>1.00</td>
<td>0.05</td>
<td>0.20</td>
<td>0.20</td>
<td>0.25</td>
<td>-</td>
<td>65</td>
<td>104</td>
</tr>
</tbody>
</table>

1.2.2 Bismuth Sodium Titanate (\(\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\))-Based System

Bismuth sodium titanate (\(\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\)) was firstly discovered by Smolensky in 1960 [Smolensky, 1960]. It also has typical perovskite structure and a Curie temperature of 320\(^{\circ}\text{C}\). \(\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\) ceramic has good ferroelectric properties (\(P_r = 38 \mu\text{C/cm}^2\)), large piezoelectric coefficients, low dielectric constant (\(\varepsilon = 240 \sim 340\)), and good acoustic properties (\(N_p = 3200 \text{ Hz} \cdot \text{m}\)). But it also has a high electric conductivity, making the poling of the ceramic difficult.
Recently, Hajime _et al._ find the way out for improving the stability of Bi$_{1/2}$Na$_{1/2}$TiO$_3$ ceramic by doping [Hajime, 1998]. Till now, the stable Bi$_{1/2}$Na$_{1/2}$TiO$_3$-based system with good properties can be divided into the following structures:

1. (1-\(x\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xM\)TiO$_3$ (\(M = \text{Ba, Sr, Ca, Bi}_{1/2}\text{K}_{1/2}\), etc.)
2. (1-\(x\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xM'\)TiO$_3$ (\(M' = \text{K, Li, Na, etc.}\))
3. (1-\(x\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xABO_3\) (\(A = \text{Bi, La, etc.}, B = \text{Cr, Fe, Mn, etc.}\))
4. (1-\(x-y\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xBaTiO_3\)-\(yBaFeO_3\)
5. (1-\(x-y\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xM''\)NbO$_3$-\(y/2(Bi_2O_3\cdot Sc_2O_3)\) (\(M'' = \text{K, Na, etc.}\))
6. (1-\(x-y\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xBaTiO_3\)-\(yBi_{1/2}\text{K}_{1/2}\)TiO$_3$
7. (1-\(x\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xSrCaTiO_3\)
8. (1-\(x\)) Bi$_{1/2}$Na$_{1/2}$TiO$_3$-\(xBa[ZryTi(1-y)]O_3\)
9. (Bi$_{1/2}$Na$_{1/2}$)$_{1-x}$Ba$_x$TiO$_3$-\(ySb_2O_3\)
10. Bi$_{1/2}$Na$_{1/2}$K$_x$Liy)$_{1/2}$TiO$_3$

The properties of some Bi$_{1/2}$Na$_{1/2}$TiO$_3$-based piezoelectric ceramics are shown in Table 1.3 [Yin, 2004].
Table 1.3 Properties of Bi$_{1/2}$Na$_{1/2}$TiO$_3$-based ceramics with a second component.

<table>
<thead>
<tr>
<th>Second Component</th>
<th>$d_{33}$(pC/N)</th>
<th>$k_p$ (%)</th>
<th>$k_{33}$ (%)</th>
<th>$\varepsilon_{33}^T/\varepsilon_0$</th>
<th>$Q_m$</th>
<th>$T_c$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>125</td>
<td>-</td>
<td>57</td>
<td>1001</td>
<td>-</td>
<td>278</td>
</tr>
<tr>
<td>NaNbO$_3$</td>
<td>71.1</td>
<td>10.8</td>
<td>43.3</td>
<td>338</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BiFeO$_3$</td>
<td>-</td>
<td>20.6</td>
<td>43.8</td>
<td>618</td>
<td>861</td>
<td>440</td>
</tr>
<tr>
<td>NaSbO$_3$</td>
<td>-</td>
<td>36.8</td>
<td>49.2</td>
<td>1462</td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>BiCrO$_3$</td>
<td>-</td>
<td>31.2</td>
<td>41.7</td>
<td>155</td>
<td>1288</td>
<td>-</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>-</td>
<td>28</td>
<td>37.2</td>
<td>602</td>
<td>472</td>
<td>-</td>
</tr>
</tbody>
</table>

1.2.3 Alkaline Niobate-Based System

The research on alkaline niobate-based piezoelectric system began from NaNbO$_3$-KNbO$_3$ ceramic. This system has low density, high mechanical quality factor $Q_m$, high electron mechanical coupling coefficient $k_p$, small dielectric constant, and good piezoelectric properties. It can be used as photoelectric applications and high frequency transducers. But alkaline is easily volatized in air, thus it is hard to obtain a alkaline niobate-based ceramics with good quality by traditional ceramic fabrication methods. This problem has not been solved until doping techniques are used in the system. Since then, many application researches of alkaline niobate-based piezoelectric ceramics have been carried out.
The alkaline niobate-based piezoelectric ceramic system has the following structures:

1. \((1-x)\) NaNbO\(_3\)-xABO\(_3\) (A = K, Li, Na, etc., B = Nb, Ta, Sb, etc.)
2. \((1-x)\) NaNbO\(_3\)-xA’Nb\(_2\)O\(_6\) (A’ = Mg, Mn, Ca, Sr, Ba, Bi\(_{1/2}\) Ag\(_{1/2}\), Bi\(_{1/2}\) Na\(_{1/2}\), etc.)
3. \((1-x)\) NaNbO\(_3\)-xA’TiO\(_3\) (A’ = Mg, Mn, Ca, Sr, Ba, Bi\(_{1/2}\) Ag\(_{1/2}\), Bi\(_{1/2}\) Na\(_{1/2}\), etc.)
4. Li\(_x\)Ag\(_{1-x}\)NbO\(_3\)
5. (Li, Na, K) (Nb, R) O\(_3\) (R = Ta, Sb, etc.)
6. KNbO\(_3\)-based alkaline niobate system

The properties of some alkaline niobate-based system piezoelectric ceramic systems are shown in Table 1.4 [Yin, 2004].

<table>
<thead>
<tr>
<th></th>
<th>tanδ</th>
<th>Q(_m)</th>
<th>(k_p) (%)</th>
<th>(k_{33}) (%)</th>
<th>(d_{33})(pC/N)</th>
<th>T(_c)(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(<em>{0.5})K(</em>{0.5})NbO(_3)+0.01mol%CuO</td>
<td>0.45</td>
<td>1661.9</td>
<td>38.9</td>
<td>-</td>
<td>-</td>
<td>415</td>
</tr>
<tr>
<td>Li(<em>{0.1})(Na(</em>{0.5})K(<em>{0.5}))(</em>{0.9})(Nb(<em>{0.8})Ta(</em>{0.2}))O(_3)</td>
<td>0.007</td>
<td>360</td>
<td>33.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sr(<em>{1.9})Ca(</em>{0.1})Nb(<em>5)O(</em>{15})+2wt%La(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Sr(<em>{1.9})Ca(</em>{0.1})NaNb(<em>5)O(</em>{15})+1wt%Nd(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>225</td>
<td>-</td>
</tr>
<tr>
<td>Sr(<em>{1.9})Ca(</em>{0.1})NaNb(<em>5)O(</em>{15})+1wt%Y(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>230</td>
<td>-</td>
</tr>
<tr>
<td>Li(<em>{0.04})Na(</em>{0.48})K(<em>{0.48})(Nb(</em>{0.9})Ta(_{0.1}))O(_3)</td>
<td>-</td>
<td>-</td>
<td>46.5</td>
<td>-</td>
<td>-</td>
<td>~400</td>
</tr>
</tbody>
</table>
1.3 Bismuth Layer-Structured Ferroelectrics (BLSF)

Bismuth layer structure was discovered by Aurivillius [Aurivillius, 1949]. The general formula is \((\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}\), built up by the regular intergrowth of \((\text{Bi}_2\text{O}_2)^{2+}\) layers and perovskite \((\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}\) slabs along the pseudotetragonal c axis, where A-site can be mono-, di-, or trivalent ions, such as \(	ext{Bi}^{3+}, \text{La}^{3+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}, \text{Na}^+, \text{K}^+\), or a mixture of them, B-site represents \(	ext{Nb}^{5+}, \text{Ta}^{5+}, \text{Ti}^{4+}, \text{W}^{6+}, \text{Mo}^{6+}, \text{Cr}^{3+}, \text{Zr}^{4+}\), etc., or a mixture of them, and \(m\) is an integer usually lying in the range from 1 to 5.

Bismuth layer-structured compounds that have ferroelectricity are named as bismuth layer-structured ferroelectrics (BLSF). BLSF are potential candidates for electronic applications because they have the following merits as compared with PZT and other lead-free materials:

1. low dielectric constant,
2. high Curie temperature,
3. low temperature coefficients of the resonant frequency,
4. strong anisotropic electromechanical coupling factor, and
5. low aging rate.

Based on these characteristics, BLSF ceramics can be used as piezoelectric devices that to be operated at high temperatures and high frequencies. In the following sections, some typical BLSF are introduced separately.
1.3.1 MBi$_4$Ti$_4$O$_{15}$-based BLSF

When Ti$^{4+}$ is at the B-site of $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, $(\text{M}^{2+}^{1/3}\text{Bi}^{3+}_{2/3})$ at A-site, and $m$ equals 4, $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ becomes MBi$_4$Ti$_4$O$_{15}$, where M can be Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, etc. MBi$_4$Ti$_4$O$_{15}$-based piezoelectric ceramic is one of the most important bismuth layer-structured piezoelectric ceramics, the patents of it is near 40% of those for all the bismuth layer-structured piezoelectric ceramics [Lin, 2003]. CaBi$_4$Ti$_4$O$_{15}$ is one of the most useful MBi$_4$Ti$_4$O$_{15}$-based piezoelectric ceramics. CaBi$_4$Ti$_4$O$_{15}$ ceramic has a very high Curie temperature of 790°C, but low piezoelectric coefficient which can be improved by adding metallic oxides. In CaBi$_4$Ti$_4$O$_{15}$, A-site Ca$^{2+}$ in $(\text{Ca}^{2+}_{2/3}\text{Bi}^{3+}_{1/3})$ can be replaced by di-, or trivalent metal ions except Ca$^{2+}$ and Bi$^{3+}$, while B-site Ti$^{4+}$ can be replaced by Si$^{4+}$ and W$^{6+}$. Metallic oxides are also added into CaBi$_4$Ti$_4$O$_{15}$ to improve the properties. Tables 1.5-1.7 show properties of CaBi$_4$Ti$_4$O$_{15}$-based piezoelectric ceramics.
### Table 1.5 Properties of the modified CaBi$_4$Ti$_4$O$_{15}$ ceramics [Lin, 2003].

<table>
<thead>
<tr>
<th></th>
<th>wt %</th>
<th>$T_c$ (°C)</th>
<th>$d_{33}$ (pC/N)</th>
<th>tanδ (%)</th>
<th>$Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaBi$_4$Ti$<em>4$O$</em>{15}$</td>
<td>98.24~98.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$WO$_6$</td>
<td>1.71~2.18</td>
<td>865~875</td>
<td>14.0~16.1</td>
<td>0.23~0.37</td>
<td>3817~5230</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.05~0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaBi$_4$Ti$<em>4$O$</em>{15}$</td>
<td>95.94~94.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$WO$_6$</td>
<td>3.86~5.60</td>
<td>870~875</td>
<td>12.8~14.2</td>
<td>0.34~0.64</td>
<td>2417~42304</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.2~0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 1.6 Properties of Ca$_{1-x}$M$_1$$_x$Bi$_4$Ti$_4$O$_{15}$ and Ca$_{1-x}$M$_{22/3}$$_x$Bi$_4$Ti$_4$O$_{15}$ with MnCO$_3$ ceramics [Lin, 2003].

<table>
<thead>
<tr>
<th>M1</th>
<th>M2</th>
<th>x</th>
<th>y</th>
<th>density (g/cm$^3$)</th>
<th>resistivity (Ω·cm)</th>
<th>$k_t$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>6.75</td>
<td>$2.0 \times 10^{11}$</td>
<td>7.4</td>
</tr>
<tr>
<td>Sr</td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>6.92</td>
<td>$4.0 \times 10^{13}$</td>
<td>16.9</td>
</tr>
<tr>
<td>Ba</td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>6.97</td>
<td>$3.0 \times 10^{13}$</td>
<td>17.9</td>
</tr>
<tr>
<td>La</td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>6.90</td>
<td>$8.0 \times 10^{12}$</td>
<td>15.9</td>
</tr>
<tr>
<td>Nd</td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>6.91</td>
<td>$8.0 \times 10^{12}$</td>
<td>16.0</td>
</tr>
<tr>
<td>-</td>
<td>La</td>
<td>0.15</td>
<td>0.5</td>
<td>6.89</td>
<td>$7.0 \times 10^{12}$</td>
<td>17.4</td>
</tr>
<tr>
<td>-</td>
<td>Nd</td>
<td>0.15</td>
<td>0.5</td>
<td>6.85</td>
<td>$7.0 \times 10^{12}$</td>
<td>17.8</td>
</tr>
</tbody>
</table>
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Table 1.7 Properties of (Ca_{1-x}M_x)Bi_4(Ti_{1-y}Ny)_4O_{15} with MnCO_3 ceramics

[Lin, 2003].

<table>
<thead>
<tr>
<th>M</th>
<th>N</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>k_t (%)</th>
<th>f,Tc (10^{-6}/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>W</td>
<td>0</td>
<td>0.5</td>
<td>1.5</td>
<td>14.9</td>
<td>34.8</td>
</tr>
<tr>
<td>Sr</td>
<td>W</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>19.1</td>
<td>37.3</td>
</tr>
<tr>
<td>Ba</td>
<td>W</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>15.9</td>
<td>37.0</td>
</tr>
<tr>
<td>La</td>
<td>W</td>
<td>0.2</td>
<td>0.1</td>
<td>0.5</td>
<td>19.2</td>
<td>30.1</td>
</tr>
<tr>
<td>Y</td>
<td>W</td>
<td>0.3</td>
<td>0.1</td>
<td>0.5</td>
<td>20.5</td>
<td>25.3</td>
</tr>
<tr>
<td>Sr</td>
<td>Si</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>20.7</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>Si</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
<td>21.0</td>
<td>-</td>
</tr>
</tbody>
</table>

SrBi_4Ti_4O_{15} is another important MBi_4Ti_4O_{15}-type piezoelectric ceramic. Like CaBi_4Ti_4O_{15}-based piezoelectric ceramics, adding metal oxides such as MnO, MnO_2, or MnCO_3 into SrBi_4Ti_4O_{15} piezoelectric ceramics can effectively improve the properties. Moreover, after replace part of Sr^{2+} in A-site by La^{3+} or some mixed compounds, one can obtain a number of SrBi_4Ti_4O_{15}-based piezoelectric ceramics with high Curie temperature ( > 450°C). Figures 1.3 and 1.4 show the dependences of properties of (Sr_{1-x}La_x)Bi_4Ti_4O_{15} ceramics on the content of La.
Figure 1.3 Dependence of electromechanical coupling factor $k_t$ and mechanical quality factor $Q_m$ on composition of $(\text{Sr}_{1-x}\text{La}_x)\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ceramics [Lin, 2003].

Figure 1.4 Dependence of Curie temperature $T_c$ on composition of $(\text{Sr}_{1-x}\text{La}_x)\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ceramics [Lin, 2003].
1.3.2 SrBi$_2$Nb$_2$O$_9$-based BLSF

SrBi$_2$Nb$_2$O$_9$ piezoelectric ceramic has a Curie temperature of 440°C, high mechanical quality factor $Q_m$ of 577, and electromechanical coupling factor $k_t$ of 10% to 16.5%; but the sintering temperature is quite high, over 1250°C. Replacing Sr in A-site by Ca, Ba, La, etc. can change the Curie temperature and sintering temperature, while the replacement of Nb in B-site by W or Si can enhance the mechanical quality factor $Q_m$. On the other hand, by replacing both A- and B-site ions piezoelectric ceramics with good piezoelectric properties can be produced, e.g. $M_1xSr_{1-x}Bi_2(Nb_{1-y}N_y)O_9$ and $M_2\frac{2x}{3}Sr_{1-x}Bi_2(Nb_{1-y}N_y)O_9$, where $M_1$ and $M_2$ are metal ions except Sr and Bi, $N$ represents W or Si.

1.3.3 Mixed BLSF System

A number of mixed BLSF systems have been prepared, by combining two or three $(Bi_2O_2)^{2+}(A_{m-1}B_mB_{m+1})^{2-}$ of various A, B and m together. Most of them exhibit good piezoelectric properties (Table 1.8). Similar studies are being continued to find out more useful lead-free piezoelectric candidates.
Table 1.8 Properties of mixed bismuth layer-structured piezoelectric ceramics

[Lin, 2003].

<table>
<thead>
<tr>
<th>Composition</th>
<th>$d_{33}$ (pC/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(CaBi_2Nb_2O_9)<em>x(CaBi_2Ta_2O_9)</em>{1-x}$ ($x=0.2$--$0.6$)</td>
<td>10--15</td>
</tr>
<tr>
<td>$(Bi_3TiNbO_9)<em>x(Bi_3TiTaO_9)</em>{1-x}$ ($x=0.2$--$0.6$)</td>
<td>13</td>
</tr>
<tr>
<td>$(SrBi_4Ti_4O_{15})<em>x(BaBi_4Ti_4O</em>{15})_{1-x}$ ($x=0.2$--$0.6$)</td>
<td>28--40</td>
</tr>
<tr>
<td>$(BaBi_2Ta_2O_9)<em>x(Bi_3TiTaO_9)</em>{1-x}$ ($x=0.2$--$0.6$)</td>
<td>10</td>
</tr>
<tr>
<td>$(BaBi_2Nb_2O_9)<em>x(CaBi_2Ta_2O_9)</em>{1-x}$ ($x=0.4$)</td>
<td>45</td>
</tr>
<tr>
<td>$(SrBi_2Ta_2O_9)<em>x(SrBi_2Nb_2O_9)</em>{1-x}$ ($x=0.3$)</td>
<td>80</td>
</tr>
</tbody>
</table>
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1.4 Bismuth Titanate-Based Ferroelectrics

1.4.1 Bismuth Titanate (BT)

Among the bismuth layer-structured ferroelectrics, bismuth titanate (BT), Bi$_4$Ti$_3$O$_{12}$, is the most important and has attracted considerable attention in recent years. It is a typical ferroelectric material with useful properties for optical memory, piezoelectric and electro-optic devices [Wu, 1976].

The crystal structure of Bi$_4$Ti$_3$O$_{12}$ is shown in Figure 1.5. It also has an Aurivillius structure and the symmetry is pseudotetragonal. The crystal structure of Bi$_4$Ti$_3$O$_{12}$ can be described as a stacking of layers of Bi$_2$O$_2$ and Bi$_2$Ti$_3$O$_{10}$ along c axis. In the Bi$_2$Ti$_3$O$_{10}$ units, Ti ions are enclosed by oxygen octahedral, which are linked through corners forming O-Ti-O linear chains. Bi ions occupy the spaces in the framework of TiO$_6$ octahedral. Thus, Bi$_2$Ti$_3$O$_{10}$ units possess a remarkable similarity to the perovskite-type structure. The height of the perovskite-type layer sandwiched between Bi$_2$O$_2$ layers in Bi$_4$Ti$_3$O$_{12}$ is equal to six Ti-O distances or approximately to three ABO$_3$ perovskite units [Subbarao, 1961].
Figure 1.5 One half of the pseudotetragonal unit cell of Bi$_4$Ti$_3$O$_{12}$

A denotes the perovskite layer Bi$_2$Ti$_3$O$_{10}^{2-}$, C denotes the Bi$_2$O$_2^{2+}$ layer, and B is the unit cell of the hypothetical perovskite structure BiTiO$_3$ [Subbarao, 1961].
Bismuth titanate is potentially useful for memory application because of its low dielectric permittivity, high Curie temperature \( T_c = 948K \) \cite{Jovalekic, 1998}, and high dielectric breakdown strength. Compared to the other ferroelectric ceramics such as BaTiO\(_3\), Pb(Zr,Ti)O\(_3\), etc., the high Curie temperature of Bi\(_4\)Ti\(_3\)O\(_{12}\) makes it useful over a wider temperature range, either for standard electronic elements such as ceramics capacitors, piezoelectric transducers, sensors, etc., or new ones, such as high-density dynamic random access memories (DRAMs) and nonvolatile memories. The spontaneous polarization vector in BT is in the \( a-c \) plane at an angle of about 4.5 to the \( a \) axis, and exhibits two independently reversible components \cite{Cummins, 1968}. One is along the \( a \) axis \( P_s = 50 \mu C/cm^2 \), and the other is along the \( c \) axis \( P_s = 4 \mu C/cm^2 \). The low coercive field along the \( c \) axis makes BT an attractive gate electrode material for ferroelectric field effect transistor (FET) devices of nondestructive readout (NDRO) mode \cite{Gu, 1996}.

Although Bi\(_4\)Ti\(_3\)O\(_{12}\) is such a good candidate for high temperature applications, its fatigue properties are not so good. It is suggested that the simple charge-compensating role of the Bi\(_2\)O\(_2^{2+}\) layers is not sufficient to make it fatigue free \cite{Park, 1999}. Moreover, because of the plate-like crystal structure and the limited number of permissible orientations for the spontaneous polarization, it is difficult to achieve high density and high piezoelectric activity \cite{Hong, 2000}.
1.4.2 Oxygen Vacancies in Bismuth Titanate

Being non-polar (paraelectric) above Curie temperature but spontaneously polarized (ferroelectric) below it, ferroelectric perovskites offer a tantalizing potential for applications: large actuation through domain switching and memory storage via switchable electric polarization. Oxygen vacancies, commonly present and mobile at high temperature, are the primary defects and thus play a central role in these applications.

This is typically the case in thin films where oxygen loss at high temperature is quenched into the room temperature. When oxygen is lost, it exits the crystal as neutral O\(_2\), leaving behind two electrons. The vacancy thus behaves as a donor. At room temperature, many of these electrons are thermally freed from the vacancy sites. In the case of ceramics, oxygen vacancies can also become mobile at high temperature during fabrication.

Moreover, XPS studies on pure bismuth titanate ceramic discovered that, oxygen vacancies neighboring bismuth ions are more likely inside the Bi\(_2\)O\(_2\) layer than in the perovskite BiTiO\(_3\) structure \[Jovalekic, 1998\]. It is suggested that in the perovskite portion of the Bi\(_4\)Ti\(_3\)O\(_2\) structure, the Bi and Ti cations share oxygen atoms in the BiTiO\(_3\) unit cell. The strong Ti–O bonds in the perovskite lattice are not easily broken implying a nonrandom distribution of oxygen vacancies and their confinement inside the Bi\(_2\)O\(_2\) layer.
1.4.3 Doping Effects in Bismuth Titanate

To further investigate the fatigue problem in Bi$_4$Ti$_3$O$_{12}$, X-ray Diffraction (XRD) technique has been used for deep study of the crystal structure. In Bi$_4$Ti$_3$O$_{12}$ thin films, oxygen vacancies are found at both the Bi$_2$O$_2^{2+}$ and Bi$_2$Ti$_3$O$_{10}^{2-}$ perovskite layers. It appears that the chemical stability of the perovskite layers against oxygen vacancies may be the reason for the fatigue resistance [Park, 1999]. Based on this theory, element ions have been doped into Bi$_4$Ti$_3$O$_{12}$ to replace part of the Bi ions near the Ti-O octahedron layers. A schematic diagram of lanthanum (La)-doped Bi$_4$Ti$_3$O$_{12}$ is shown in Figure 1.6.

![Diagram of La-doped Bi$_4$Ti$_3$O$_{12}$](image)

Figure 1.6 Lattice structure of La-doped Bi$_4$Ti$_3$O$_{12}$ [Park, 1999].
The doping of La for Bi in Bi$_4$Ti$_3$O$_{12}$ has been proved to be successful. For a capacitor made of Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ (BLT) thin film, the polarization-electric field (P-E) curve does not show any serious asymmetric behavior resulting from imprint failures after $3 \times 10^{10}$ read/write cycles at a frequency of 1M Hz and the value of polarization remains nearly constant after repetitive read/write cycles [Park, 1999]. Compared with Bi$_4$Ti$_3$O$_{12}$, the fatigue resistance is evidently improved. Doping makes Bi$_4$Ti$_3$O$_{12}$ become a potential candidate for non-volatile memory devices.

Besides, the remnant polarization of BLT thin film is obviously larger than that of BT thin film. It is reported that in Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$, the rotation of TiO$_6$ octahedral in the a-b plane accompanied with a shift of the octahedron along the a axis is largely enhanced by the lanthanoid element doping for Bi in the pseudoperovskite layer [Ngochi, 2001]. Since this enhance is mainly caused by the ionic radius difference between La and Bi, a replacement for Bi by an element with a smaller ionic radius than La in the pseudo-perovskite layer is expected to improve the ferroelectric properties more. This is further supported by the experimental results of Bi$_{3.44}$Nd$_{0.56}$Ti$_3$O$_{12}$. Kojima et al. showed that the remanent polarization ($P_r$) of Bi$_{3.44}$Nd$_{0.56}$Ti$_3$O$_{12}$ was larger than that of Bi$_{3.44}$La$_{0.56}$Ti$_3$O$_{12}$ (25 µC/cm$^2$ and 17 µC/cm$^2$) [Kojima, 2002]. The ionic radius of La$^{3+}$ is 1.06 Å while that of Nd$^{3+}$ is 1.00 Å.
Like other bismuth layer-structured systems, Bi$_4$Ti$_3$O$_{12}$ has the layer-typed crystal structure that can be described as (Bi$_2$O$_2$)$_{2+}$($A_{m-1}B_mB_{3m+1}$)$_{2-}$. Thus, the doping in Bi$_4$Ti$_3$O$_{12}$ can also be divided by A-site doping for replacing Bi, and B-site doping for replacing Ti. Both La- and Nd-doping belong to A-site doping which results in enhancement in fatigue resistance and ferroelectric properties. Table 1.9 lists some of the mostly used elements to be doped into Bi$_4$Ti$_3$O$_{12}$ and their ionic radius.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionic Radius (Å)</th>
<th>Element</th>
<th>Ionic Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (4+)</td>
<td>0.68</td>
<td>Bi (3+)</td>
<td>0.96</td>
</tr>
<tr>
<td>Nb (4+)</td>
<td>0.74</td>
<td>Ca (2+)</td>
<td>0.99</td>
</tr>
<tr>
<td>V (3+)</td>
<td>0.74</td>
<td>La (3+)</td>
<td>1.06</td>
</tr>
<tr>
<td>Mo (6+)</td>
<td>0.62</td>
<td>Nd (3+)</td>
<td>1.00</td>
</tr>
<tr>
<td>W (6+)</td>
<td>0.62</td>
<td>Pr (3+)</td>
<td>1.01</td>
</tr>
<tr>
<td>Cr (3+)</td>
<td>0.63</td>
<td>Y (3+)</td>
<td>0.89</td>
</tr>
<tr>
<td>Mn/Fe (3+)</td>
<td>0.66</td>
<td>Sm (3+)</td>
<td>0.96</td>
</tr>
<tr>
<td>Mn/Fe (4+)</td>
<td>0.60</td>
<td>Dy (3+)</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Watanabe et al. studied La-V and Nd-V doping in Bi$_4$Ti$_3$O$_{12}$ [Watanabe, 2002] and had a complete report on the functions of A- and B-site doping separately which was finally defined as Site-Engineering. In the theory of site-engineering, the B-site doping is explained to eliminate the vacancy defects and reduce the influence of domain pinning. This theory was then validated by experimental results of La-W and La-Mo doping in bismuth titanate ceramics [Wang, 2004] and La-Nb doping by Song et al. [Song, 2004].

According to the site-engineering theory, A-site doping in BLSF generally leads to the formation of anti-phase boundaries (APBs), offering more nucleation sites for new domain and curve 90° domains which increase the mobility of domain. In addition, with A-site doping, there will be an increase in the jumping activation energy of the oxygen vacancies which will lead to a decrease in the mobility of oxygen vacancies, domain pinning is thus reduced and the fatigue resistance is consequently improved. On the other hand, B-site doping mainly decreases the concentration of oxygen vacancies, thereby reducing domain pinning and enhancing the remnant polarization. Sometimes B-site doping with ions of different ionic radius may also increase the remnant polarization for the structure distortion of the oxygen octahedral.

Subbarao et al. reported that the Curie temperature increases with the decreasing of the ionic radius in A-site doping, i.e., a smaller cation benefits more to the Curie temperature $T_c$ [Subbarao, 1961]. Concluding from the experimental
results, the A- and B-site cations in the perovskite layers are readily to be replaced by a large number of element ions. The A-site doping is more effective than that of B-site doping, because the cations in B-sites are too similar in size and does not play the major structural role in the polarization process for BLSF [Frit, 1992].

In general, lead-free materials have lower piezoelectric coefficients than lead-based ones. Among the lead-free materials, BT-based ceramics has the lower ferroelectric and piezoelectric properties, but they have the highest Curie temperature, which makes them applicable in high-temperature applications. In addition, the dielectric constant of BT-based ceramics is low, this also makes the ceramics suitable for use in sensor applications.

Table 1.10 Properties of some BT-based piezoelectric ceramics.

<table>
<thead>
<tr>
<th>M</th>
<th>x</th>
<th>ε</th>
<th>E_c(kV/cm)</th>
<th>P_r(µC/N)</th>
<th>d_{33}(pC/N)</th>
<th>T_c(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La^1</td>
<td>0.15</td>
<td>150</td>
<td>50</td>
<td>12</td>
<td>~10</td>
<td>~600</td>
</tr>
<tr>
<td>Nd^2</td>
<td>0.5</td>
<td>130</td>
<td>50</td>
<td>19</td>
<td>~20</td>
<td>~650</td>
</tr>
<tr>
<td>V^3</td>
<td>0.06</td>
<td>140</td>
<td>80</td>
<td>20</td>
<td>-</td>
<td>~650</td>
</tr>
<tr>
<td>Nb^4</td>
<td>0.01</td>
<td>175</td>
<td>65</td>
<td>15</td>
<td>15</td>
<td>~600</td>
</tr>
</tbody>
</table>

The properties of BT ceramics doped with different elements are shown in Table 1.10. It is clearly seen that Nd-doped BT ceramic has better ferroelectric and electronic properties than La- and V-doped BT ceramics. It is suggested that the improved ferroelectric properties and electrical resistance of rare earth-doped bismuth titanate oxides are arisen from the increased structural distortion of the pseudoperovskite layers (i.e. the rotation of TiO$_6$ octahedral in the a-b plane accompanied with a shift of the octahedra along the $a$ axis), so the doping of a smaller ion, i.e. Nd, should result in a larger remanent polarization and better piezoelectric properties.

On the other hand, it has also been shown that doping of niobium (Nb) into BT ceramics can reduce oxygen vacancies and thus influence the electrical leakage and fatigue resistance of the bismuth titanate thin films [Wang, 2004]. Besides, the piezoelectric properties of BT ceramics can also be improved by the doping of Nb.

On the basis of these findings, neodymium (Nd)-modified bismuth titanate has been chosen as the base composition for the present work, and niobium (Nb) will be further doped to improve the electric, dielectric, ferroelectric, piezoelectric and pyroelectric properties. The general formula of the BT ceramic with Nd- and Nb-doping is Bi$_{3.5-x/3}$Nd$_{0.5}$Ti$_{3-x}$Nb$_x$O$_{12}$ (BNTN). The resulting effect of the Nb doping will be investigated and the associated mechanism will be discussed.
1.5 Scope of Work

This main objective of present work is to develop proper composition of lead-free ferroelectric oxides with good piezoelectric and pyroelectric properties for various microelectromechanical systems (MEMS) applications especially at high temperatures, and also to explore the effects of rare earth ions doping in bismuth layer-structure ferroelectric system.

Following the introduction, there are five main parts in this thesis:

Chapter 2: Fabrication and characterization of BNTN ceramics
Chapter 3: Dielectric and leakage current properties of BNTN ceramics
Chapter 4: Ferroelectric, piezoelectric and pyroelectric properties of BNTN ceramics
Chapter 5: Fabrication and properties of BNT thin films
Chapter 6: Conclusions

In Chapter 2, the fabrication process of the BNTN ceramics will be introduced in details. To judge the quality of the ceramics, the densities of BNTN ceramics are measured. X-ray diffraction (XRD) technique is used to confirm the crystalline structures of the ceramics. Scanning electron microscopy (SEM) is employed to study the cross-sectional microstructures of the ceramics.
In Chapter 3, the dielectric and leakage current properties of the BNTN ceramics are measured. The experimental techniques and procedures are briefly explained. To explore the effect of the Nb-doping in BNT system, all the results are discussed. The dielectric properties by temperature are measured and the behavior of the ceramics under high temperature is studied.

In Chapter 4, the ferroelectric, piezoelectric and pyroelectric properties of the BNTN ceramics are measured. The experimental techniques and procedures are briefly explained. To explore the effect of the Nb-doping in BNT system, all the results are discussed.

In Chapter 5, BNT ferroelectric thin films are fabricated by sol-gel method. The Fabrication and characterization of the films are briefly introduced. The dielectric, ferroelectric, pyroelectric and piezoelectric of the films are measured and discussed.

In Chapter 6, the conclusions and suggestions for future work are given.
Chapter Two

Fabrication and Characterization of BNTN Ceramics

2.1 Fabrication of BNTN Ceramics

2.1.1 Preparation of BNTN Ceramics

Bismuth titanate-based ceramics, $\text{Bi}_{3.5-x/3}\text{Nd}_{0.5}\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ with $x$ varying from 0 to 0.09 (abbreviated as BNTN-100x), were prepared by a conventional mixed-oxide technique using commercially available oxide powders. The fabrication procedure can be describes as follows:

1. Weight the commercially available oxides $\text{Bi}_2\text{O}_3$ (99%), $\text{TiO}_2$ (99%), $\text{Nb}_2\text{O}_3$ (99.99%), and $\text{Nd}_2\text{O}_5$ (99.99%) accurately to give a composition of $\text{Bi}_{3.5-x/3}\text{Nd}_{0.5}\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ (abbreviated as BNTN-100x). Mix them together in a mortar.

2. Put the roughly mixed oxide powders in the ball milling machine. Mix them well in alcohol using Y$_2$O$_3$-stablized zirconia balls, the milling time is usually larger than 20 hours.

3. After ball milling, take the mixture of alcohol and oxide powders out and dry it up in an oven at a temperature of over 80°C for 2 to 3 hours.
(4) Put the powders in a crucible and heat it at 800°C for 6 hours for calcinations. The temperature profile is shown in Figure 2.1.

(5) After calcinations, ball-mill the powders thoroughly again in alcohol. Then dry it in an oven at 80°C for 2-3 hours.

(6) After drying, mix it thoroughly with a PVA binder solution. Then uniaxially press the powder into disk samples with a diameter of 10 mm and a thickness of 0.6 mm.

(7) Sinter the disk samples at 1000°C for 4 hours in air. The temperature profile is shown in Figure 2.2.

The flowchart for fabricating the BNTN ceramics is shown in Figure 2.3. The ceramic samples prepared in the present work are listed in Table 2.1.
Figure 2.1 Temperature profile for calcinating the BNTN ceramics.

Figure 2.2 Temperature profile for sintering the BNTN ceramics.
Weighed oxide powders:
- Bi$_2$O$_3$ (99%), TiO$_2$ (99%)
- Nb$_2$O$_3$ (99.99%), Nd$_2$O$_5$ (99.99%)

Ball milling in alcohol for over 20 hours

Calcination at 800°C for 6 hours.

Ball milling in alcohol for over 20 hours.

Pressed into disk samples.

Sintering at 1000°C for 4 hours.

Bi$_{3.5-x/3}$Nd$_{0.5}$Ti$_{3-x}$Nb$_x$O$_{12}$

(x = 0, 0.03, 0.06, 0.09)

Ceramics

Figure 2.3 Fabrication procedures for the BNTN ceramics.
Table 2.1 The BNTN ceramic samples prepared in the present work.

<table>
<thead>
<tr>
<th>Ceramic Formula</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₃.5Nd₀.5Ti₃O₁₂</td>
<td>BNTN-0</td>
</tr>
<tr>
<td>Bi₃.₄₉Nd₀.₅Ti₂.₉₇Nb₀.₀₃O₁₂</td>
<td>BNTN-3</td>
</tr>
<tr>
<td>Bi₃.₄₈Nd₀.₅Ti₂.₉₄Nb₀.₀₆O₁₂</td>
<td>BNTN-6</td>
</tr>
<tr>
<td>Bi₃.₄₇Nd₀.₅Ti₂.₉₁Nb₀.₀₉O₁₂</td>
<td>BNTN-9</td>
</tr>
</tbody>
</table>

Sintering temperature is very important to ceramics. For bismuth titanate ceramics, the sintering temperature is usually higher than 1100°C. However, because of the change in crystal structure after doping, the sintering temperature for BT-based ceramics is reduced to around 1000°C [Lin, 2003]. It has also been shown that the sintering temperature does not change too much for BT-based ceramics added with different amounts of dopants.

In the present work, the BNTN ceramics were sintered in a temperature range of 900°C to 1100°C in order to determine the optimum sintering temperature. Since it was found that the density which is usually used to indicate the densification of the ceramics did not change significantly in the tested temperature range, the dielectric properties as well as piezoelectric and pyroelectric properties were also measured for determining the optimum sintering temperature. Since doping level does not affect the sintering temperature of BT-based ceramics, only BNTN-6 samples were used for determining the optimum sintering temperature for the BNTN ceramics.
Table 2.2 shows the electrical, dielectric, ferroelectric, piezoelectric and pyroelectric properties of the BNTN-6 ceramic sintered at different temperatures. The measurements of each property will be discussed in the following chapters. As shown in Table 2.2, it is clearly seen that the ceramic sintered at 1000°C has not only the dense structure, but also the best electrical, piezoelectric and pyroelectric properties. Therefore, all the BNTN ceramics were sintered at 1000°C in the present work.
Table 2.2 Density ($\rho$), dielectric constant ($\varepsilon$), dielectric loss (tan$\delta$), remanent polarization ($P_r$), coercive field ($E_c$), longitudinal piezoelectric coefficient ($d_{33}$), pyroelectric coefficient ($p$) and leakage current density ($J$) of the BNTN-6 ceramic sintered at different temperatures.

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$ (g/cm$^3$)</td>
<td>7.9</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>$\varepsilon$ (1 kHz)</td>
<td>92</td>
<td>106</td>
<td>110</td>
</tr>
<tr>
<td>tan$\delta$ (%) (1 kHz)</td>
<td>2.0</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>$P_r$ (µC/cm$^2$)</td>
<td>6</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>$E_c$ (kV/cm)</td>
<td>80</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>$d_{33}$ (pC/N)</td>
<td>19</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>$p$ (µC/m$^2$K)</td>
<td>89</td>
<td>132</td>
<td>115</td>
</tr>
<tr>
<td>$J$ (A/cm$^2$)</td>
<td>$5\times10^{-7}$</td>
<td>$6\times10^{-8}$</td>
<td>$9\times10^{-8}$</td>
</tr>
</tbody>
</table>
2.1.2 Deposition of Top Electrodes

Gold (Au) electrodes were deposited on the top and bottom surfaces of the sintered samples by DC magnetron sputtering in a pure-argon (Ar) pressure for the subsequent poling and measurements.

Figure 2.4 Schematic diagram of the magnetron sputtering chamber [Kwok, 2003].
Figure 2.4 shows the schematic diagram of the magnetron sputtering chamber. There are three magnetron sputtering guns (Kurt J. Lesker, TORUS 2C) in the sputtering chamber. For this study, two DC powered sputtering guns were used. A metal gold (Au) disc (Kurt J. Lesker, purity 99.99%) of diameter 2 inch and 0.125 inch thickness was used as the sputtering targets. The DC magnetron guns were mounted such that its axis made an angle of 10° with the substrate normal. The BNTN ceramic samples were placed on the substrate holder. The distance between the substrate and target was 16 cm. During the deposition period, the substrate holder was rotated to ensure the electrode is of a uniform thickness.
2.2 Characterizations of BNTN Ceramics

2.2.1 Density of BNTN Ceramics

Density is an important parameter indicating the densification as well as the degree of crystallization of the ceramics. In this work, the densities of the BNTN ceramics were measured by the liquid displacement method. It is based on Archimedes’s principle. The sample weight in air is $m_a$, the sample weight in water or liquid is $m_w$, and then the density of the sample is given by

$$\rho = \frac{m_a}{m_a - m_w} \rho_w$$

(2.1)

The schematic diagram of the liquid displacement method is shown in Figure 2.5.

![Figure 2.5 Schematic diagram of the liquid displacement method](Benjamin, 1985)
Table 2.3 Densities of the BNTN ceramic samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BNTN-0</th>
<th>BNTN-3</th>
<th>BNTN-6</th>
<th>BNTN-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$ (g/cm$^3$)</td>
<td>7.9</td>
<td>8.0</td>
<td>8.0</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 2.3 shows the densities of the BNTN ceramic samples. It can be seen that the densities of all the ceramics are roughly the same. As compared with the theoretical value for bismuth titanate (8.04 g/cm$^3$) \cite{Hong, 2000} our ceramic samples are fully densified.

2.2.2 Crystalline Structure of BNTN Ceramics

An x-ray diffractometer with nickel-filtered CuK\(\alpha\) radiation (D8 Discover, Bruker) was used to investigate the crystalline structure of the BNTN ceramics and powders. For the measurement, a parallel beam of x-ray is directed to incident on the sample surface (Figure 2.6). The diffracted beam is received by a detector which is driven to scan from $2\theta = 20^\circ$ to $60^\circ$. When the Bragg’s law is satisfied, constructive interference occurs in the diffracted beam and a high-intensity signal is resulted. The Bragg’s law is given as:

$$\lambda = 2d \sin \theta$$

(2.2)
Figure 2.6   Diffraction of x-rays by planes of atoms [Chung, 1992].

The x-ray diffraction (XRD) pattern of the BNTN-0 ceramic powder is shown in Figure 2.7. The diffraction patterns are indexed with bismuth titanate ceramics. It is seen that because of the diffuse reflection on the rough surface of the powder, most of the diffraction peaks are too weak to be observed. Nevertheless, among the weak peaks, the peak associated with (117) plane has the highest intensity. It has been reported that the highest intensity of the diffraction peak (11[*]) is consistent with the fact that the most intense reflection of BLSF are all of the type of (11[2m+1]) [Du, 1998].

XRD patterns of the BNTN-0, BNTN-3, BNTN-6 and BNTN-9 ceramics are shown in Figure 2.8. As comparing to the XRD pattern of the BNTN-0 powder shown in Figure 2.7, all the BNTN ceramics show no significant structural difference in the diffraction peaks; all exhibit a well crystallized phase with diffraction peaks attributable to the BT-layered perovskite structure.
Figure 2.7 XRD pattern of the BNTN-0 powder.

Figure 2.8 XRD patterns of the BNTN ceramics.
2.2.3 Microstructure of BNTN Ceramics

Scanning electron microscope (SEM) is an instrument that can be used to examine the microstructure of a wide range of materials. In this work, a scanning electron microscope (Leica Stereoscan 440) was used to examine the cross section of the BNTN ceramics. Figures 2.9-2.12 show the SEM micrographs of the cross section of the BNTN ceramics. It can be seen that all the BNTN ceramics have a dense structure, consisting of plate-like grains randomly oriented in the matrix.

![Figure 2.9 SEM micrograph of the cross section of the BNTN-0 ceramic](image)
Figure 2.10 SEM micrograph of the cross section of the BNTN-3 ceramic

Figure 2.11 SEM micrograph of the cross section of the BNTN-6 ceramic
On the basis of all the above results, including high density, XRD with single perovskite phase and dense structures, it can be concluded that the BNTN ceramics were well sintered at 1000°C for 4 hours.
Chapter Three
Dielectric and Leakage Properties of BNTN Ceramics

3.1 Dielectric Properties of BNTN Ceramics

As mentioned in Chapter 1, the study of lead-free piezoelectric materials has been carried out for long time. Among all the lead-free piezoelectric materials, bismuth titanate (BT) is considered to be a potential candidate for high temperature applications. However, it has been shown that BT has a very high conductivity and leakage current which make the poling of the ceramic difficult and thus limit its use in various applications. To overcome the problem, different ions have been doped into the BT system. In general, most of the doping could reduce the oxygen vacancies and hence improve the dielectric properties and leakage of BT.

In this chapter, the effects of Nb doping on the dielectric properties and leakage current of the BNTN ceramics will be investigated. The resulting effect on oxygen vacancies will also be studied. A system including a HP 4192A impedance analyzer and a high-temperature furnace was used to measure the dielectric properties in the temperature range of 100°C to 650°C and frequency range of 10 Hz to 1 MHz, while another system including a dielectric spectrometer (NOVOCtrl BDS 40) and a cryosystem (NOVOCtrl Quatro Cryosystem)
was used to measure the dielectric properties in the temperature range of 23°C to 400°C and frequency range of 1 mHz to 1 MHz. The leakage current density is measured by a Keithley 6517A electrometer/high resistance meter.

Figure 3.1 shows the variations of the dielectric constant (ε) and dielectric loss (tan δ) at 1 kHz of the BNTN ceramics with Nb doping level x. It can be seen that the dielectric constant decreases by about 15% as x increases from 0 to 0.03 and then remains almost unchanged at x > 0.03. Familiar with ε, the dielectric loss tan δ decreases by about 20% as x increases from 0 to 0.03, and then slowly increases to 0.009 when x = 0.09 which is 90% of the value when x = 0 (without Nb doping).
Figure 3.1 Variations of the dielectric constant ($\varepsilon$) and dielectric loss ($\tan \delta$) at 1 kHz of the BNTN ceramics with the Nb doping level $x$. 
3.2 Curie Temperature of BNTN Ceramics

Most ferroelectric materials undergo a structural phase transition from a high temperature non-ferroelectric (or paraelectric) phase into a low temperature ferroelectric phase. The paraelectric phase may be piezoelectric or nonpiezoelectric and is rarely polar. The symmetry of the ferroelectric phase is always lower than the symmetry of the paraelectric phase. The temperature of the phase transition is called the Curie temperature, $T_C$. Above the Curie temperature the permittivity falls off with temperature according to the Curie–Weiss law:

$$\varepsilon = \varepsilon_0 + \frac{C}{T-T_0} \approx \frac{C}{T-T_0}$$  \hspace{1cm} (3.1)

where $C$ is the Curie constant, $T_0$ ($T_0 < T_C$) is the Curie–Weiss temperature.

Some ferroelectrics, such as barium titanate, BaTiO$_3$, undergo several phase transitions into successive ferroelectric phases. Only the temperature associated with the transition into the first ferroelectric phase is called Curie temperature. The transition into a ferroelectric phase usually leads to strong anomalies in the dielectric, elastic, thermal and other properties of the material and is accompanied with changes in the dimensions of the crystal unit cell. Some changes that can occur in a ferroelectric material which transforms from a paraelectric cubic into a ferroelectric tetragonal phase are illustrated in Figure 3.2.
Figure 3.2 Illustration of the changes in a ferroelectric material which transforms from a paraelectric cubic into ferroelectric tetragonal phase with temperature. Such a phase transition is observed in BaTiO$_3$ and PbTiO$_3$. The permittivity curve represents data measured on a BaTiO$_3$ ceramic. The arrows show possible directions of the spontaneous polarization (in two dimensions). The unit cell is represented by a square in the cubic phase and rectangle in the tetragonal phase \cite{Damjanovic,1998}.

As a phase transition temperature, Curie temperature is very important to the ferroelectrics since it defines the upper limit of the service temperature range in which the ferroelectric materials function as a ferroelectric. Since it is expected that the BNTN ceramics are potential candidates for high-temperature sensor applications, it is of great interest and need to study the temperature dependence of \( \varepsilon \) for the ceramics.
Figure 3.3 Variations of the dielectric constant ($\varepsilon$) of the BNTN ceramics by temperature with different Nb doping level $x$.

Table 3.1 Curie temperatures of the BNTN ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>BNTN-0</th>
<th>BNTN-3</th>
<th>BNTN-6</th>
<th>BNTN-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (°C)</td>
<td>532</td>
<td>545</td>
<td>537</td>
<td>524</td>
</tr>
</tbody>
</table>
Figure 3.3 shows the temperature dependence of the dielectric constant at 1 kHz for all the BNTN ceramics, while Table 3.1 lists the Curie temperatures of them. As known in Figure 3.3, the observed dielectric constant of all the BNTN ceramics with different Nb doping levels exhibit similar dependence on temperature and reach a similar maximum value at around 540°C. Attributed to the high Curie temperature of bismuth titanate ceramic, the Curie temperature of all the ceramics are quite high. Among the ceramics, the BNTN-3 ceramic has the highest Curie temperature of 545°C, which is about 2% higher than the BNTN-0 ceramic (without Nb-doping).

The high Curie temperature of the BNTN ceramics ensured that they can be used for high-temperature applications. The change in Curie temperature caused by Nb-doping can be explained by the decrease in lattice distortion of the perovskite layers (Subbarao, 1961), while the similar temperature dependence show that the Nb-doping does not change the microstructure of the BNTN ceramics too much.

Figure 3.4 shows the temperature dependence of dielectric constant ($\varepsilon$) at different frequencies for the BNTN-3 ceramic. It is seen that the temperature dependence remains similar at different testing frequencies. Similar behavior have been observed in the BNTN ceramics with different Nb doping levels.
Figure 3.4 Temperature dependence of dielectric constant ($\varepsilon$) at different frequencies for the BNTN-3 ceramic.
3.3 Oxygen Vacancies in BNTN Ceramics

In the studies of ferroelectric materials studies, oxygen vacancy is always an important problem. Several models have been built, based on the experimental observations, to explain the oxygen vacancy effect on the conductivity and polarization of the ferroelectrics. Shulman et al. pointed out that the oxygen vacancy concentration is critical to the dielectric relaxation observed in bismuth titanate ceramics, which shows classic characteristic of an oxygen-ion-jump process [Shulman, 2000]. This relaxation can also be found in single crystals in the absence of grain boundaries. They also showed that Nb-doping could suppress the relaxation through the suppression of oxygen vacancies as well as their mobility (because of the increase in the hopping barrier and hence the activation energy for oxygen vacancies).

Similar work have also been carried out by Li et al. [Li, 2004]. In their studies on bismuth titanate ceramics, they measured the temperature dependence of the dielectric loss at different frequencies under vacuum condition. At 10 Hz, a dielectric loss peak with the relaxation-type characteristic was observed at about 100°C. As frequency increased, the dielectric loss peak shifted towards high temperatures. They suggested that it was associated with the migration of oxygen vacancies inside ceramics. Based on the Debye theory and the Cole-Cole fitting, they showed that there existed a strong correlation among oxygen vacancies, which was considered to commonly exist among oxygen vacancies in ferroelectrics. In
fact, Yao et al. have also carried out similar investigation on the dielectric loss peak observed in bismuth titanate ceramics [Yao, 2004]. By fitting the experimental data to the Arrehenius relation $\tau = \tau_0 \exp(U/k_BT)$ (where $\omega\tau = (\varepsilon_s/\varepsilon_\infty)^{1/2}$, $\tau$, $U$, $\varepsilon_s$, $\varepsilon_\infty$, are the relaxation time, activation energy, static dielectric permittivity and high frequency dielectric permittivity, respectively), they further confirmed that the dielectric peak was associated with the hopping of oxygen vacancies.

To provide further convincing connection between the dielectric loss and oxygen diffusion, Li et al. compared the dielectric loss peak of bismuth titanate ceramics treated in the way that its oxygen vacancies concentration was either increased or decreased [Li, 2004]. For the ceramics with high oxygen vacancy concentration, by annealing under reducing atmosphere (97% Ar and 3% H₂ mixed air) at a temperature of 600°C for 20 hours, the dielectric loss peak increased in magnitude. On the other hand, for the ceramics with lower oxygen vacancy concentration, by dipping in oxydol ambient (H₂O₂) for 20 hours, the dielectric loss peak decreased in magnitude. At last, they suggested that the magnitude of the dielectric loss peak was proportional to the oxygen vacancy concentration.

In the study of bismuth titanate, people found out that oxygen vacancies are responsible for the high conductivity of the materials and also lead to a high leakage current which makes the ceramics difficult for poling [Yao, 2004]. To reduce the oxygen vacancies, Nb ions are usually doped, The introduction of the Nb⁵⁺ at the Ti⁴⁺ site as donor impurities can effectively reduce the oxygen vacancies and then suppress the dielectric loss peak. In this section, the effects of oxygen vacancies on
dielectric properties are discussed, and the resulting effects on the ferroelectric, piezoelectric and pyroelectric properties will be discussed in Chapter 4.

First, the BNTN-3 ceramic was used as an example to investigate the effects of oxygen vacancies on the dielectric loss. Based on the results, the effects of Nb-doping on the oxygen vacancies are then discussed in the following section. Following the work of Li et al., the temperature dependence of the dielectric loss in the frequency range of 5 mHz to 1 MHz were measured, and the results are shown in Figure 3.5. It should be noted that our measurements were carried out under atmospheric pressure, instead of under vacuum. As shown in Figure 3.5a, dielectric loss peaks are observed in the temperature of 200°C to 300°C for frequency lower than 10 Hz. In general, the loss peak shifts towards low temperatures as frequency decreases. This is consistent with the work of Li et al. However, different from the results of Li et al., the loss peak occurs at higher temperatures and increase in magnitude as frequency decreases. Moreover, there is no dielectric loss peak observed in the temperature range up to 400°C at frequencies higher than 10 Hz (Figure 3.5b). This may be partly due to the doping effect (Nd and Nb) and partly due to the difference in testing environment (atmospheric pressure vs. vacuum). It has been reported that the La and Nb doping could increase the activation energy for oxygen vacancies [Shulman, 2000; Yao, 2004].
Figure 3.5 Temperature dependence of dielectric loss ($\tan \delta$) of the BNTN-3 ceramic at different measuring frequencies.
Following the works of Shulman et al. [Shulman, 2000] and Li et al. [Li, 2004], the BNTN-3 ceramic were treated by the following two processes in sequence:

1. Reducing Gas Treatment. The BNTN-3 ceramic is annealed at 400°C for 4 hours in an argon atmosphere under a base pressure of $1 \times 10^{-3}$ Pa to reduce the oxygen content in the ceramic. This process is to drive the oxygen ions in the ceramic away, and thus produce more oxygen vacancies.

2. Oxydol Treatment. The BNTN-3 ceramic was dipped in oxydol ambient ($H_2O_2$) for 40 hours and then baked at 100°C for 30 minutes. Since oxydol ambient has a strong oxygenation, this process is to fill oxygen into the ceramic to reduce the content of oxygen vacancies. The baking process at 100°C is to remove the excess water.

After the treatment, the temperature dependence of the dielectric loss was measured. Figure 3.6 shows the temperature dependence of the dielectric loss at 0.1 Hz for the BNTN-3 ceramic treated by the process1 (Reducing Gas Treatment) as well as that for the as-prepared ceramic for comparison. It can be seen that after the treatment by which oxygen vacancies are introduced, the dielectric loss peak becomes much larger and the magnitude increases by more than 60%.
Figure 3.6 Temperature dependence of dielectric loss (tan δ) of the BNTN-3 ceramic after different treatments (at frequency 0.1 Hz).
To provide further evidence on the effect of oxygen vacancies, the treated BNTN-3 ceramic was further treated by the process 2 (Oxydol Treatment) to reduce the content of oxygen vacancies. The temperature dependence of the dielectric loss at 0.1 Hz for the treated ceramic was measured and shown also in Figure 3.6 for comparison. It is clearly seen that the dielectric loss peak of the ceramic decreases almost to the original value after the treatments. On basis of the above results, it can be observed that oxygen vacancies exists in the BNTN-3 ceramic and have effects on the dielectric loss similar to those in bismuth titanate ceramics.

In this work, the frequency dependence of the dielectric loss for the BNTN ceramics has also been measured at room temperature to study the effects of oxygen vacancies. The experimental result for the as-prepared BNTN-3 ceramic is shown in Figure 3.7. It can be seen that the dielectric loss remains almost unchanged at a small value of about 0.01-0.02 in the frequency from 1 kHz to 1 mHz. Besides of the DC conduction effect, it is suggested that the increase in dielectric loss at low frequencies is attributed to the motion of oxygen vacancies. This suggestion is supported by the measurements on the ceramic treated by process 1 and 2 (Figure 3.7). For the BNTN-3 ceramic treated by process 1 (Reducing Gas Treatment) to increase the oxygen vacancy concentration, the dielectric loss is larger than that of the as-prepared ceramic at each frequency in the whole tested frequency range; and the difference increases as frequency decreasing and reaches a maximum of about ten times at 1 mHz. However, after the treated ceramic has been further treated by process 2 (Oxydol Treatment) to reduce the oxygen vacancy content, the dielectric loss decreases almost to the original value.
Figure 3.7 Variations of the dielectric loss ($\tan \delta$) of the BNTN-3 ceramics after different treatments.
3.4 Niobium Doping Effects on Oxygen Vacancies in BNTN Ceramics

Based on the results on the effects of oxygen vacancies on the dielectric loss mentioned in the above section, the effects of Nb-doping on oxygen vacancies are investigated by the means of the dielectric loss measurements in this section.

Figure 3.8 shows the temperature dependence of the dielectric loss at 1 Hz for the BNTN ceramics with different Nb doping levels. It is clearly seen that, after the doping of Nb, the dielectric loss peak shifts towards high temperatures, indicating that the activation energy is increased. On the other hand, the Nb-doping reduces the amplitude of the dielectric loss peak. In terms of the amplitude of the loss peak or the oxygen vacancy concentration, the optimum doping level of Nb is around 3 mol% to 6 mol%. It should be noted that, if simply in terms of room-temperature dielectric loss at 1 kHz, it is hard to determine the optimum doping level of Nb as there exists only slight difference.
Figure 3.8 Variations of the dielectric loss of the BNTN ceramics with temperature by different Nb doping levels (at frequency 1 Hz).
3.5 Leakage Current of BNTN Ceramics

The leakage current density (J) for the BNTN ceramics with different Nb doping level x is shown in Figure 3.9. It can be seen that the observed J decreases with increasing x and reaches a minimum value of about $3 \times 10^{-8}$ A/cm$^2$ at x = 0.06. Li et al. reported that the leakage current flowing through a ferroelectric ceramic comprises of two components: polarization contribution and leakage contribution. Under low electric fields (< 40kV/cm), the leakage current increases linearly with increasing electric field. This indicates that the contact barrier limits current injection and consequently thermally excited electrons are the dominant source of current. As the electric field increases, oxygen vacancies and other particles in the materials obtain enough energy to participate in electric conduction [Li, 2004]. In this work, the leakage current density is measured under an electric field of 75 kV/cm which is much higher than 40 kV/cm. Hence, we suggest that the observed variation in J can reveal the real changing trend of oxygen vacancies and such other loss factors in Nb-doped BNT ceramics. In fact, this is in consistent with our results on the dielectric loss discussed in the last section. The oxygen vacancy concentration was effectively reduced by the doping of Nb, which is exemplified by the decrease in the amplitude of the dielectric loss peak.
Figure 3.9 Variation of the leakage current density $J$ of the BNTN ceramics with Nb doping level $x$. 
4.1 Ferroelectric Properties of BNTN Ceramics

Ferroelectrics are polar materials that possess at least two equilibrium orientations of the spontaneous polarization vector in the absence of an external electric field, and in which the spontaneous polarization vector may be switched between those orientations by an electric field. This reversibility is a consequence of the fact that the polar structure of a ferroelectric crystal is a slightly distorted non-polar structure. In general, uniform alignment of electric dipoles (spontaneous polarization) only occurs in certain regions of a crystal, while in other regions of the crystal electric dipoles may be in the reverse direction (such as twinning). Such a region with uniform polarization is called a ferroelectric domain. The interface between two domains is called domain wall. The spontaneous polarization of a domain may be reversed by the application of a strong electric field. This dynamic process of reversing the domain is called domain switching, and the process depends on temperature and the applied electric field [Batthias, 1948]. The relation between the net macroscopic polarization of a ferroelectric material and the applied electric field is manifested as a polarization hysteresis (P-E) loop.
A typical polarization hysteresis (P-E) loop of a (111)-oriented 1.3-µm thick sol-gel-derived PZT45/55 (PbZr$_{0.45}$Ti$_{0.55}$O$_3$) film is shown in Figure 4.1 [Damjanovic, 1998]. When a small electric field (positive) is applied, the polarization increases linearly with the field amplitude. This shows as segment AB in the figure. In this region, the field is not strong enough to switch domains with the unfavorable direction of polarization. As the field is increased, the polarization of domains with an unfavorable direction of polarization will start to switch in the direction of the field, rapidly increasing the measured charge density (segment BC). And the polarization response in this region is strongly nonlinear. Once all the domains are aligned (point C), the ferroelectricity again behaves linearly (segment CD). If the field strength starts to decrease, some domains will back-switch, but at zero fields the polarization is nonzero (point E). To reach a zero polarization state, the field must be reversed (point F). Further increase of the field in the negative direction will cause a new alignment of dipoles and saturation (point G). The field strength is then reduced to zero and reversed to complete the cycle.

In this process, the value of polarization at zero fields (point E) is called the remanent polarization, $P_r$. The field required to bring the polarization to zero is called the coercive field, $E_c$. The spontaneous polarization $P_s$ is usually taken as the intercept of the polarization axis with the extrapolated linear segment CD. It should be mentioned that the coercive field $E_c$ that is determined from the intercept of the polarization hysteresis (P-E) loop with the field axis is not an absolute threshold field. If a low electric field is applied over a (very) long time period, the polarization will eventually switch [Damjanovic, 1998].
A Sawyer-Tower bridge is one of the typical experimental setups for measuring the polarization hysteresis (P-E) loop of a ferroelectric material. Figure 4.2 shows the schematic circuit for the Sawyer-Tower bridge [Sawyer and Tower, 1930]. A function generator (HP 8116A, Hewlett-Packard) is used to supply an alternating voltage $V_{ac}$, which is then amplified by 2000 times using a power amplifier (TREK model 20/20A amplifier) before applying to the sample. The actual voltage applied to the sample is measured using an oscilloscope (HP 54645A, Hewlett-Packard), from which the electric field applied to the sample is calculated. A reference capacitor with capacitance $C_o$ is connected in series with the sample.
$C_0$ is usually much larger (about 1000 times) than the capacitance of the sample, so that it can store the polarization charges generated during the polarization switching but without affecting the process. Accordingly, the change of the polarization $P$ of the sample can be calculated from the voltage $V$ across the reference capacitor, which is measured using the oscilloscope, by

$$P = \frac{C_0 V}{A}$$

(4.1)

where $A$ is the electrode area. The plot of $P$ versus $E$ gives a polarization hysteresis (P-E) loop of a ferroelectric material. In the present work, an AC field at 100 Hz was applied to the ceramic samples. The AC field was increased constantly until a saturated polarization hysteresis (P-E) loop was obtained.

Figure 4.2 Schematic circuit of Sawyer-Tower bridge for the observation of P-E characteristics in ferroelectrics [Sawyer and Tower, 1930].
Figure 4.3 shows the polarization hysteresis (P-E) loops of the BNTN ceramics with different Nb doping level x, while their remanent polarization $P_r$ and coercive field $E_c$ determined from these loops are shown in Figure 4.4. All the polarization hysteresis (P-E) loops were obtained under a maximum electric field of 130 kV/cm. It can be seen that the observed $P_r$ increases significantly from 9 $\mu$C/cm$^2$ to 15 $\mu$C/cm$^2$ as x increases from 0 to 0.06; it then decreases at x larger than 0.06. On the other hand, the observed $E_c$ decreases with increasing x, and reaching a minimum value of about 75 kV/cm at x = 0.06. On the basis of these results, it is clearly shown that the Nb dopant can affords improvement in the ferroelectric properties of BNT ceramics and the optimum doping level is around 6 mol%. Since Nb$^{5+}$ ion is larger than Ti$^{4+}$ ion (0.0640 nm vs. 0.0605 nm), the doping will increase the structural distortion of oxygen octahedral, hence lead to an increase in $P_r$ [Yao, 2004]. It is also suggested that the decrease in oxygen vacancies caused by the doping of Nb may reduce domain pinning and hence enhance $P_r$ [Song, 2004].
Figure 4.3 Polarization hysteresis (P-E) loops of the BNTN ceramics.
Figure 4.4 Variations of the remanent polarization $P_r$ (●) and coercive $E_c$ (□) of the BNTN ceramics with Nb doping level $x$. 
4.2 Poling of BNTN Ceramics

Due to the complex set of elastic and electric boundary conditions at each grain, ferroelectric grains in ceramics and polycrystalline films are always split into many domains. If the direction of the spontaneous polarization through the material is random or distributed in such a way as to lead to zero net polarization, the pyroelectric and piezoelectric effects of individual domains will cancel each other and such a material is neither pyroelectric nor piezoelectric. Ferroelectric materials may be brought into a polar state by applying a strong electric field, usually at elevated temperatures. This process, called poling, cannot orient grains, but can reorient domains within individual grains in the direction of the field. A poled ferroelectric exhibits pyroelectric and piezoelectric properties, even if many domain walls are still present. As grown ferroelectric single crystals usually contain many domains and may exhibit weak piezoelectric and pyroelectric properties. A single crystal that does not contain domains is said to be in a single-domain or monodomain state. The single-domain state in single crystals may be achieved by poling.

Figure 4.5 shows a polycrystalline ferroelectric with random orientation of grains before and after poling. In this figure, many domain walls are present in the poled material; however, the net remanent polarization is nonzero. What must be mentioned is that poling is possible only in ferroelectric materials. A pyroelectric or piezoelectric polycrystalline material with randomly oriented grains cannot be poled and exhibit pyroelectric or piezoelectric properties [Damjonovic, 1998].
As mentioned before, in a hysteresis process, the polarization of the ferroelectrics changed when the electric field changed. Based on the definition of poling, the ferroelectric material after a whole polarization hysteresis (P-E) loop measurement is actually poled by the applied electric field. Since the voltage used in the polarization hysteresis (P-E) loop measurement is alternating, this kind of poling is usually called AC-poling.

Besides AC-poling, there is another poling process called DC-poling. In this process, a DC voltage is applied to the ferroelectric materials to change the polarization directions. DC-poling is usually applied to ferroelectric samples before the pyroelectric and piezoelectric measurements. In the present work, the BNTN ceramic samples were poled under a DC field of 70 kV/cm at 200 °C in a silicon oil bath for 30 minutes. The piezoelectric and pyroelectric measurements were carried out 2-3 days after the samples were poled.
4.3 Piezoelectric Properties of BNTN Ceramics

The piezoelectric effect or piezoelectricity is an interaction between the electrical and mechanical systems. The (direct) piezoelectric effect is manifested by the change of the electric polarization under the application of a mechanical stress, and is quantified with a piezoelectric coefficient $d_{ip}$ which is defined as

$$d_{ip}^E = \frac{\partial D_i}{\partial T_p} |_{E}$$

where $D$ is the electric displacement, $E$ is the electric field and $T$ is the stress, $i = 1, 2, 3$ and $p = 1, 2… 6$.

In 1881, a year after the discovery of the direct piezoelectric effect, Lippmann predicted the existence of the converse effect from a thermodynamic approach [Ikeda, 1990]. The converse piezoelectric effect is manifested by the induction of the strain under the application of an electric field, and is quantified with a piezoelectric coefficient $d_{pi}^T$ which is defined as

$$d_{pi}^T = \frac{\partial S_p}{\partial E_i} |_{T}$$

where $S$ is the elastic strain.
It has been shown that the piezoelectric coefficients $d_{ip}^E$ and $d_{pi}^T$ were thermodynamically identical [Ikeda, 1990; Damjanovic, 1998], i.e.

$$d_{ip}^E = d_{pi}^T$$  \hspace{1cm} (4.4)

Before the end of the same year, the Curie brothers verified the prediction of Lippmann and also showed that the piezoelectric coefficients $d_{ip}^E$ and $d_{pi}^T$ of quartz had the same values [Ikeda, 1990].

In the present work, the longitudinal piezoelectric coefficient $d_{33}$ was measured using a $d_{33}$ meter (ZJ-38, Institute of Acoustics Academica Sinica). The photograph of the $d_{33}$ meter is shown in Figure 4.6. The $d_{33}$ meter provides a direct means of testing piezoelectric materials. The $d_{33}$ meter clamps the sample under test, and then subjects it to a low frequency (110 Hz) oscillatory force. Processing of the electrical signals from the sample and comparison with a built-in reference enables the system to give a direct reading of $d_{33}$. This method of testing offers superior resolution and consistency as compared to static methods of testing. Unlike resonance methods, it is appropriate to almost any sample geometry. All that is required is an electroded area where one can apply the force and collect the charge.
Figure 4.6 ZJ-3B $d_{33}$ meter.

Figure 4.7 Variations of the longitudinal piezoelectric coefficient $d_{33}$ with Nb doping level $x$. 
Figure 4.7 shows the variations of $d_{33}$ values of the BNTN ceramics with Nb doping level $x$. It can be seen that the observed $d_{33}$ increase with increasing $x$, reaching a maximum value of 22 pC/N at $x = 0.06$. This is very similar to the variation in the remanent polarization $P_r$ (Figure 4.4), but the increment is smaller. For $d_{33}$, the increment from the minimum value at $x = 0.00$ to the maximum value at $x = 0.06$ is about 30%, while that in $P_r$ value is about 100%. This difference may be understood in terms of the equation [Damjanovic, 1998]:

$$d = 2\varepsilon Q P_s$$

(4.5)

where $d$ is the piezoelectric coefficient, $\varepsilon$ is the dielectric constant, $Q$ is the electrostrictive coefficient, and $P_s$ is the spontaneous polarization. The spontaneous polarization can be estimated by the remanent polarization determined in previous section. It can be seen that $d$ is not only dependent on $P_s$, but also on $\varepsilon$ and $Q$. As discussed in Chapter 3, the observed $\varepsilon$ for the ceramics decreases by about 15% as the doping level increases from 0 to 6 mol%. Hence, the small increment in $d_{33}$ should be attributed to the decrease in $\varepsilon$ at the same time. The electrostrictive coefficient is mainly dependent on the elastic properties of the ceramic, so it could be assumed almost constant for ceramics with different Nb doping levels.

Based on Equation 4.5, one can also see that the piezoelectric (charge) coefficient $d$ is greatly dependent on $\varepsilon$. Probably because of this, the observed $d$ for the BNTN ceramics is very small as compared to that for lead-based piezoelectric ceramics. For example, the $\varepsilon$ and $d$ values of a PZT-4 ceramic are about 1300 and 290 pC/N, respectively, while those of the BNTN-6 ceramic are 99 and 22 pC/N.
Nevertheless, if the piezoelectric (voltage) coefficient (which is proportional to the ratio of $d/\varepsilon$) is considered, the BNTN ceramics become comparable to the lead-based ceramics. Therefore, the BNTN ceramics are potential candidate for replacing the lead-based ceramics for sensor applications.
4.4 Pyroelectric Properties of BNTN Ceramics

Pyroelectricity originates from the temperature dependence of the spontaneous polarization. When the temperature of a crystal is changed, electric charges induced by the change of spontaneous polarization appear on the surface of the crystal. Hence, the pyroelectric coefficient \( p \) is defined as:

\[
p = \frac{\partial P_s}{\partial T'} = -\frac{1}{A} \frac{\partial Q'}{\partial T'} = -\frac{1}{A} \frac{\partial Q'}{\partial t}
\]

where \( P_s \) is the spontaneous polarization, \( T' \) is the temperature, \( A \) is the electrode area of the sample, \( Q' \) is the charge on the surface of the sample caused by the change of the temperature and \( t \) is the time.

In the present work, a Peltier element, controlled by a digital lock-in amplifier (SR830 DSD, Stanford Research System), was used to heat the sample sinusoidally around a setting temperature \( T'_0 \) the frequency \( f \) and amplitude \( T'_\omega \):

\[
T' = T'_0 + T'_\omega e^{i\omega t}
\]

where \( \omega (=2\pi f) \) is the angular frequency. The rate of change of the temperature was:

\[
\frac{dT'}{dt} = i\omega T'_\omega e^{i\omega t}
\]

Since \( T' \) varied with time sinusoidally, the resulting pyroelectric current \( I \) was also varying with time sinusoidally at the same frequency:
where \( I_0 \) is the amplitude of the pyroelectric current. Substituting Equation 4.8 and 4.9 into Equation 4.6, the pyroelectric coefficient \( p \) is given:

\[
p = -\frac{I_0}{\omega Ai T_i}
\]  

To ensure the sample was heated uniformly, a low frequency of 5m Hz was used. The amplitude of the temperature change was 1°C. The short circuit current induced on the sample was amplified by an electrometer (617 Programmable Electrometer, Keithley) and measured by the digital lock-in amplifier. The pyroelectric coefficient \( p \) was then calculated using the component of the observed current 90° out of phase with the temperature variation (Equation 4.10). Figure 4.8 shows the schematic diagram of the setup for the dynamic measurement of the pyroelectric coefficient.
Figure 4.8 Schematic diagram of the setup for the dynamic measurement of the pyroelectric coefficient [Cheung, 2003].

Figure 4.9 shows the variations of pyroelectric coefficient $p$ of the BNTN ceramics with Nb doping level $x$. It can be seen that the observed $p$ increases with increasing $x$, reaching a maximum value of $129 \, \mu$C/m$^2$K at $x = 0.06$. This is very similar to the variations in the remanent polarization $P_r$ (Figure 4.4) and piezoelectric coefficient $d_{33}$ (Figure 4.7). Although $p$ is defined as the change of the spontaneous polarization with increasing temperature, it can still provide vital evidence of the magnitude of the spontaneous polarization of a ferroelectric ceramic. So, the increment in $p$ should be arisen from the enhancement of $P_r$ by the doping of
Different from $d_{33}$, the observed $p$ for the BNTN ceramics is not very small as compared to a lead-based ferroelectric ceramic. Moreover, if the voltage figure of merit $f_v$ for pyroelectricity, which is equal to the ratio of $p/\varepsilon$, is considered, the BNTN ceramics become comparable to the lead-based ceramics. For example, the $p$ and $\varepsilon$ values for a PZT ceramic are about 290 and 380 $\mu$C/m$^2$K, respectively [Muralt, 2001], while those for the BNTN-6 ceramic are about 99 and 129 $\mu$C/m$^2$K. Therefore, the BNTN ceramics are potential candidate for replacing the lead-based ceramics for sensor applications.

![Figure 4.9 Variations of the pyroelectric coefficient $p$ of the BNTN ceramics with Nb doping level $x$.](image)

Figure 4.9 Variations of the pyroelectric coefficient $p$ of the BNTN ceramics with Nb doping level $x$.  

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4.5 Annealing Effect of BNTN Ceramics

As discussed in Chapter 3, the BNTN ceramics have very high Curie temperature (~ 540°C) and hence should be useful for high temperature applications. In this section, the high-temperature annealing effects on the piezoelectric properties of the ceramics were investigated so as to demonstrate that the ceramics could be employed in high temperature applications. Since all the ceramics with different Nb doping levels have almost the same Curie temperature, the BNTN-6 ceramic has been used as an example for this investigation. It should be noted that the BNTN-6 ceramic has the best piezoelectric properties.

In this study, the ceramic was first annealed at various high temperatures for 10 minutes, then its piezoelectric coefficient $d_{33}$ were measured at room temperature using the $d_{33}$ meter. Figure 4.10 shows the piezoelectric coefficient of the ceramic after annealing at various temperatures. It can be seen that the observed $d_{33}$ of the ceramic decreases only slightly with increasing annealing temperature, from a value of 22 pC/N for an as-poled sample to a value of 19 pC/N after the annealing at 400°C, indicating that thermal depoling is not significant for the ceramic up to 400°C. So it can anticipate that the BNTN ceramics could function effectively at high temperatures.
Figure 4.10 Effect of annealing temperature on $d_{33}$ of the BNTN-6 ceramic.
4.6 Summary

In this chapter, the hysteresis behavior, piezoelectric and pyroelectric properties of the BNTN ceramics have been discussed, and their properties are summarized in Table 4.1. At 6 mol% Nb-doping level, the ceramic shows a saturated polarization hysteresis (P-E) loop with a large remnant polarization of 15 μC/cm² and a low coercive field of 75 kV/cm. The BNTN-6 ceramic also exhibits a large piezoelectric (charge) coefficient of 22 pm/V as well as a large pyroelectric coefficients of 129 μC/m²K. On the basis of these good properties, the BNTN ferroelectric ceramic is a potential candidate for sensing applications.

Table 4.1 Properties of the BNTN ceramics by Nb doping level x.

<table>
<thead>
<tr>
<th>X</th>
<th>( P_r ) (μC/cm²)</th>
<th>( E_c ) (kV/cm)</th>
<th>( d_{33} ) (pC/N)</th>
<th>( p ) (μC/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9</td>
<td>100</td>
<td>17</td>
<td>97</td>
</tr>
<tr>
<td>0.03</td>
<td>14</td>
<td>80</td>
<td>21</td>
<td>122</td>
</tr>
<tr>
<td>0.06</td>
<td>15</td>
<td>75</td>
<td>22</td>
<td>129</td>
</tr>
<tr>
<td>0.09</td>
<td>9</td>
<td>90</td>
<td>19</td>
<td>120</td>
</tr>
</tbody>
</table>
Chapter Five
Fabrication and Properties of BNT Thin Films

5.1 Fabrication of BNT Thin Films

As mentioned in Chapter 1, among the single-element-doped bismuth titanate films, the Bi$_{3.44}$Nd$_{0.56}$Ti$_3$O$_{12}$ film has the largest remanent polarization (25 µC/cm$^2$). Based on the discussions in previous chapters, it is anticipated that the Bi$_{3.44}$Nd$_{0.56}$Ti$_3$O$_{12}$ film, owing to the large remanent polarization, should also exhibit good piezoelectric and pyroelectric properties. Together with the advantage of high Curie temperature, it should also be suitable for various high-temperature piezoelectric and pyroelectric MEMS applications. However, most of the studies on bismuth titanate-based films were focused on their ferroelectric properties and fatigue resistance for FeRAM applications. There is a lack of the knowledge of their piezoelectric and pyroelectric properties. Therefore, in this chapter, bismuth titanate-based ceramic films are prepared and their piezoelectric and pyroelectric properties are studied.
There are a number of deposition techniques for thin film fabrication. They can be classified into evaporation methods (i.e. thermal evaporation and electron-beam evaporation), gas-phase chemical processes (i.e. chemical vapor deposition and laser-enhanced chemical vapor deposition), glow-discharge processes (i.e. magnetron sputtering and ion beam deposition) [Seshan, 2002]. Among all these methods, the sol-gel method is selected for fabricating the films in the present work because of its use of simple fabrication equipment, short fabrication cycles and low cost. The sol-gel method can offer better stoichiometry control of the film composition and chemical homogeneity and produce a uniform film over a large area.

The basic processes of the sol-gel method are to form a solution of the elements of the desired compound in an organic solvent, to polymerize the solution into a gel, to dry and fire the gel for removing the organic components and forming a final inorganic oxide. It is commonly known that in the sol-gel fabrication method, the sol-gel solution is most important; the chemical composition should be not too complicated to access, i.e. simple components are the best for the sol-gel solution preparation. Hence, although we have shown that Nb doping can effectively reduce oxygen vacancy content in Bi$_{3.5}$Nd$_{0.5}$Ti$_{3}$O$_{12}$ ceramics, a ceramic film of simple composition, without Nb doping, Bi$_{3.5}$Nd$_{0.5}$Ti$_{3}$O$_{12}$ (BNT) is prepared in the present work. It is believed that this will make the chemistry in preparing the precursor solution and the films simpler; such that a film of single-phase structure and good quality could be obtained.
5.1.1 Fabrication BNT Thin Films by Sol-Gel Technique

The Bi$_{3.5}$Nd$_{0.5}$Ti$_3$O$_{12}$ (BNT) thin films were prepared by sol-gel method together with the multiple-spin-coating technique. Figure 5.1 shows the flow diagram for the fabrication of the films, and Figure 5.2 shows the schematic diagram for spin-coating technique. A BNT precursor solution with 5% excess bismuth was supplied from Mitsubishi Co. Japan. Table 5.1 lists the composition of the precursor solution. The BNT precursor was first spin coated on a Pt/Ti/SiO$_2$/Si substrate which was cleaned thoroughly before at 4500 rpm for 50 seconds to obtain a thin layer of film with uniform thickness. Then the film, which was covered by a Petri dish in order to protect from any dirt in air falling onto it, was dried on a hot plate at about 300°C. The thickness of this layer of BNT film was about 90 nm. These steps were repeated two more times, followed by a heat treatment at 500°C for 10 minutes in a rapid thermal processor (RTP500) to remove the undesired materials (the organic group in the BNT precursor solution). By repeating the process a few times, a BNT film of thickness of 0.9 µm was obtained. The film was then annealed at 650°C and 700°C for half an hour in a furnace to promote crystallization.
Figure 5.1 The flow diagram for the fabrication of the BNT thin films.
Table 5.1 Composition of the BNT precursor solution (Mitsubishi Co.).

<table>
<thead>
<tr>
<th>Components</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂O₃ (Bismuth Oxide)</td>
<td>7.2</td>
</tr>
<tr>
<td>Nd₂O₃ (Neodymium Oxide)</td>
<td>0.7</td>
</tr>
<tr>
<td>TiO₂ (Titanium Oxide)</td>
<td>2.1</td>
</tr>
<tr>
<td>(HOCH₂CH₂)₂NH (2,2-Iminodiethanol)</td>
<td>5.4</td>
</tr>
<tr>
<td>C₄H₉OH (1-Butanol)</td>
<td>65</td>
</tr>
</tbody>
</table>
Figure 5.3 shows the TGA and DSC thermograms of the BNT precursor solution, measured at a heating rate of 10°C/min with a Zetzsch STA 449C Simultaneous Thermal Analyzer. It is seen that all the exothermal peaks locate at temperatures below 500°C and the mass of the sample becomes almost constant at temperature higher than 500°C. These indicate that a temperature of 500°C is high enough for the heat treatment to remove all the organic groups in the precursor solution.
Figure 5.3 DSC and TGA thermalgrams of the BNT precursor solution.
5.1.2 Deposition of Top Electrodes

For the subsequent poling and measurements, a series of gold/chromium (Au/Cr) top electrodes of diameter 0.8 mm was deposited on the film through a shadow circular mask by DC magnetron sputtering. The pattern of the electrodes is shown in Figure 5.4.

Figure 5.4 The pattern of the electrodes on the BNT thin film:
(a) Side view; (b) Top view.
The distance between the sample and the target is about 16cm. During the deposition period, the sample holder was rotated by a step motor to ensure the uniformity of the electrodes. Chromium was first deposited and followed by gold. The thickness of the gold/chromium top electrodes was measured to be 160 nm, using a surface profiler (KLA-Tencor P-10). The deposition parameters of the gold and chromium are listed in Table 5.2.

**Table 5.2 Deposition parameters for chromium and gold electrode.**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chromium (Cr)</th>
<th>Gold (Au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter Gas</td>
<td>Argon (Ar)</td>
<td>Argon (Ar)</td>
</tr>
<tr>
<td>Gas Flow Rate</td>
<td>10 sccm</td>
<td>10 sccm</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>1 Pa</td>
<td>1 Pa</td>
</tr>
<tr>
<td>Sputter Power</td>
<td>60 W</td>
<td>70 W</td>
</tr>
<tr>
<td>Sputter Time</td>
<td>3 minutes</td>
<td>5 minutes</td>
</tr>
</tbody>
</table>
5.2 Characterization of BNT Thin Films

In this section, the crystalline structure and microstructure of the BNT thin films were studied and the results were discussed.

5.2.1 Crystalline Structure of BNT Thin Films

An x-ray diffractometer with nickel-filtered CuKα radiation (D8 Discover, Bruker) was used to investigate the crystalline structure of the BNT thin films. The x-ray diffraction (XRD) patterns of the BNT thin films annealed at 650°C and 700°C are shown in Figure 5.5 and 5.6. Similar to the BNTN ceramic samples, the diffraction patterns are indexed with bismuth titanate ceramics. The XRD patterns indicate that both the films are well crystallized with a single phase of bismuth layered perovskite structure and no evidence of a secondary phase such as the fluorite phase or pyrochlore phase.
Figure 5.5 XRD pattern of the BNT thin film annealed at 650°C.

Figure 5.6 XRD pattern of the BNT thin film annealed at 700°C.
5.2.2 Microstructure of BNT Thin Films

A scanning electron microscope (Leica Stereoscan 440) was used to examine the microstructure of the BNT thin films. Figure 5.7 and 5.8 show the SEM micrographs of the cross section of the BNT thin films annealed at 650\(^\circ\)C and 700\(^\circ\)C. Although the film surface is not very smooth, the films are still quite dense. It is also seen that the grain size of the films increases as the annealing temperature increases. Similar results have also been observed by Suyal et al. [Suyal, 2002]. They further showed that owing to the increase in grain size, the remanent polarization of the BNT thin films annealed at higher temperature was increased.
Figure 5.7 SEM micrograph of the cross section of the BNT thin film annealed at 650°C.

Figure 5.8 SEM micrograph of the cross section of the BNT thin film annealed at 700°C.
5.3 Properties of BNT Thin Films

In this section, the dielectric, ferroelectric, piezoelectric and pyroelectric properties of the BNT thin films are studied. Most of the measurement techniques used for ceramic samples were applied to determine the properties of the thin film samples. For the piezoelectric properties, a special technique was used to determine the transverse piezoelectric coefficient $e_{31}$, instead of the longitudinal piezoelectric coefficient $d_{33}$, of the thin films.

5.3.1 Ferroelectric Properties of BNT Thin Films

Polarization hysteresis (P-E) loops for the BNT thin films annealed at 650°C and 700°C are shown in Figure 5.9 and 5.10, respectively. It can be seen that the remanent polarization $P_r$ of the film increases from 19 µC/cm$^2$ to 22 µC/cm$^2$ as the annealing temperature increases from 650°C to 700°C, while the coercive field $E_c$ decreases from 190 kV/cm to 170 kV/cm. These are probably due to the larger grain size. On the other hand, similar to the results for the corresponding ceramics, the observed $P_r$ and $E_c$ for both the films are larger than those of a pure BT film, indicating the effects of Nd doping.
Figure 5.9 Polarization hysteresis (P-E) loop of the BNT thin film annealed at 650°C.

Figure 5.10 Polarization hysteresis (P-E) loop of the BNT thin film annealed at 700°C.
5.3.2 Dielectric and Pyroelectric Properties of BNT Thin Films

The dielectric constant and loss at 1 kHz of the BNT thin films annealed at 650°C and 700°C are shown in Table 5.3, in which their pyroelectric coefficients are also listed. The thin films were poled under a DC field of 200 kV/cm at room temperature for 10 minutes prior to the pyroelectric as well as the piezoelectric measurements. Similar to $P_r$, the observed $p$ for the BNT thin films annealed at 700°C is larger, having a value of near 150 $\mu$C/m²K. Although it is still smaller than the value for a lead-based ferroelectric thin film, its voltage figure of merit $f_v$ for pyroelectricity, which is equal to the ratio of $p/\varepsilon$, is comparable. For example, the $f_v$ value of a PZT15/85 thin film is about 0.85 $\mu$C/m²K [Suya, 2002], while those for the BNT thin films annealed at 650°C and 700°C are about 1.10 $\mu$C/m²K and 1.35 $\mu$C/m²K, respectively. This clearly indicates that the BNT thin films can replace the lead-based ferroelectric films in sensing applications.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>650°C</th>
<th>700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ (1 kHz)</td>
<td>105</td>
<td>132</td>
</tr>
<tr>
<td>$\tan \delta$ (1 kHz)</td>
<td>0.0095</td>
<td>0.012</td>
</tr>
<tr>
<td>$p$ (µC/m²K)</td>
<td>98</td>
<td>148</td>
</tr>
</tbody>
</table>

Table 5.3 Dielectric constant ($\varepsilon$), dielectric loss ($\tan \delta$) and pyroelectric coefficient ($p$) of the BNT thin films annealed at different temperatures.
5.3.3 Piezoelectric Properties of BNT Thin Films

Besides the longitudinal piezoelectric coefficient $d_{33}$, the transverse piezoelectric coefficient $e_{31}$ is another important parameter for designing micro-electromechanical systems (MEMS). In the present work, $e_{31}$ of thin films is measured based on the direct piezoelectric effect, and the schematic diagram of the experimental setup is shown in Figure 5.11. In the measurement, a rectangular sample (film/substrate) is clamped at one end while the other end is left free. A piezoelectric actuator is used to apply a dynamic force to bend the sample. A longitudinal strain is then generated along the length of the sample ($\hat{1}$); and charges are induced on the film surface as a result of the direct piezoelectric effect. Since the film is clamped on the substrate only, it can deform freely along the thickness direction ($\hat{3}$). (In addition, the film also deforms along the width direction ($\hat{2}$) following the Poisson contraction of the substrate. Therefore, the observed transverse piezoelectric coefficient, or effective transverse piezoelectric coefficient, $e_{31,f}$ is different from the usual transverse piezoelectric coefficient $e_{31}$.)
In this $e_{31,f}$ measurement, the one end clamped rectangular sample is named cantilever. When there is a dynamic force at frequency $f$ ($=\omega/2\pi$) applied to the cantilever, the induced charge on the surface of the cantilever, due to the direct piezoelectric effect, are time varying at the same frequency $f$. For a circular top electrode on the free end of the cantilever, the induced current $I$ can be calculated by the following equation:

$$I = \frac{dQ}{dt} = \frac{3\pi r^2 \omega h z_f e_{31,f} (1 - \nu_s)}{2 \ell^3} \left[ \frac{\ell - x_0 + x_1}{2} \right]$$

(5.1)

where $r$ is the radius of the top electrode, $\omega$ ($=2\pi f$) is the frequency of the actuator, $Z_f$ is the deflection of the cantilever, $\nu_s$ is the Poisson ratio of the substrate, $h$ and $l$ are the thickness and length of the cantilever (Figure 5.12), $x_0$ and $x_1$ are the distances from the edges of the electrode to the clamped end of the cantilever (Figure 5.13).
Figure 5.12 Schematic diagram showing the bending of the cantilever [Tsang, 2002].

Figure 5.13 Schematic diagram showing the position of a top circular electrode (x is defined as the position of the electrode) [Tsang, 2002].
In the present work, a multilayer piezoelectric actuator (ASB003A, Tokin Inc.) was used to apply a dynamic force to bend the sample. The actuator was driven at a frequency \( f \) of 10 Hz using as AC drive source which consists of a function generator (HP8116A, Hewlett-Packard) and a power amplifier (BOP1000, KEPCO). The deflection \( z_f \) was measured using a photonic sensor (MTI-2000, Mechanical Technology Inc.). The current \( I \) induced on the circular top electrode was measured using a lock-in amplifier (SR830 DSP, Stanford Research Systems). Hence, the effective transverse piezoelectric coefficient \( e_{31f} \) was calculated by Equation 5.1.

For the measurement, the sample (film/substrate) is glued on a PCB. Since the top electrode is very small \( (r = 0.4 \text{ mm}) \), it is electrically connected to a large electrode pad on the PCB through a thin wire \( (\text{diameter} = 40 \text{ \( \mu \text{m} \})} \) for the ease of the measurement of the induced current. The thin wire is so long that it will not affect the bending of the cantilever. Figure 5.14 shows the sample fixture for the \( e_{31f} \) measurement.
Figure 5.14 The sample fixture for $e_{31,f}$ measurement [Tsang, 2002].

In theory, the induced current changes with position $x$ because of the different strain levels; but the $e_{31,f}$ value does not. Therefore, as a cross-check of the measurement, the $e_{31,f}$ value at different $x$ were measured. Table 5.4 shows the observed $e_{31,f}$ for the BNT thin films annealed at 650$^\circ$C and 700$^\circ$C, respectively. In calculating the $e_{31,f}$ values from the measurement of induced current $I$ (Equation 5.1), a Poisson ratio of 0.172 was used for the silicon substrate [Brantley, 1973].

As shown in Table 5.4, the observed $e_{31,f}$ for both the films does not change too much at different position $x$. This may indicate that the film are of good homogeneity and the measurement should be free from any significant systematic errors. Similar to $P_r$ and $p$, the observed $e_{31,f}$ for the BNT thin film annealed at 700$^\circ$C is larger, having a value of about 1.45 C/m$^2$. In deed, it is quite smaller than the value for a lead-based ferroelectric thin film. However, if the piezoelectric (voltage) coefficient (which is proportional to the ratio of $e/\varepsilon$) is considered, the
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Fabrication and Properties of BNT Thin Films

BNT thin films become comparable to the lead-based ones. For example, the ε and $e_{31,f}$ value for a sol-gel-derived PZT53/47 thin film are 1100 and 9.3 C/m², respectively, while those of the BNT thin film annealed at 700°C are 132 and 1.45 C/m². Again, the BNT thin films should then be a potential candidate for replacing the lead-based ferroelectric films in sensor applications.

Table 5.4 The observed $e_{31,f}$ values at different positions of the BNT films annealed at 650°C (sample 1#) and 700°C (sample 2#).

<table>
<thead>
<tr>
<th>$x$ (mm)</th>
<th>$e_{31,f}$ (C/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1#</td>
</tr>
<tr>
<td>3</td>
<td>1.15</td>
</tr>
<tr>
<td>5</td>
<td>1.07</td>
</tr>
<tr>
<td>15</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Chapter Six
Conclusions

The main objective of the present work is to study lead-free bismuth layer-structured ferroelectric materials for various high-temperature sensor applications. For environmental protection reasons, it is expected that the bismuth layer-structured ferroelectric materials can replace the currently used lead-based ferroelectric materials in various applications. In the present work, bismuth titanate-based ferroelectric materials $\text{Bi}_{3.5-x/3}\text{Nd}_{0.5}\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ (BNTN) have been prepared, and the effects of the niobium (Nb) dopant on the ferroelectric, dielectric, piezoelectric and pyroelectric properties of the ceramics have been investigated. Moreover, in order to study the feasibility of using the materials in micro-electromechanical system (MEMS), $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$ (BNT) thin films have been prepared and their piezoelectric and pyroelectric properties have been investigated.

6.1 BNTN Ceramics

Bismuth titanate-based ferroelectric ceramics, $\text{Bi}_{3.5-x/3}\text{Nd}_{0.5}\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ with $x$ varying from 0 to 0.09 (abbreviated as BNT-100x), have been successfully prepared by a conventional mixed oxide technique using commercially available...
Conclusions

The ceramic samples were sintered at 1000°C for 4 hours in air. All the BNTN ceramics were well-crystallized, showing a single phase of bismuth layered perovskite structure. No significant effects of the Nb dopant on the crystallite structure as well as the microstructure of the ceramics were observed. All the ceramics had a dense structure, consisting of plate-like grains randomly oriented in the matrix. Their densities were quite high, having a similar value of about 92% of the theoretical value.

After the doping with Nb, the dielectric constant $\varepsilon$ and $\tan\delta$ at 1 kHz decreased. However, there was no significant dependence of the observed $\varepsilon$ and $\tan\delta$ on the Nb doping level. Besides, there was no significant effect of the Nb dopant observed on the Curie temperatures ($T_c$); all the BNTN ceramics exhibited similar high values of $T_c$ ($\sim 540°C$). However, dielectric loss peaks of different magnitude at different high temperatures were observed for different BNTN ceramics. It was suggested that the dielectric loss peaks were associated with the migration of oxygen vacancies inside the ceramics and the magnitude of the loss peak was proportional to the concentration of oxygen vacancies. The Nb dopant could effectively reduce the oxygen vacancies in the ceramics, and thus leading to a dielectric loss peak of smaller magnitude. The reduction of oxygen vacancies also resulted in a smaller leakage current. For the Bi$_{3.48}$Nd$_{0.5}$Ti$_{2.94}$Nb$_{0.06}$O$_{12}$ ceramic, the observed leakage current density reached a minimum value of $3 \times 10^{-9}$ A/cm$^2$ under an electric field of 75 kV/cm.
The effects of the niobium (Nb) dopant on the ferroelectric, piezoelectric and pyroelectric properties of the BNTN ceramics have then been investigated. Our results reveal that after the doping with Nb, the observed remanent polarization $P_r$, piezoelectric (charge) coefficient $d_{33}$ and pyroelectric coefficient $p$ of the ceramics decreased, and the optimum doping level of Nb was around 6 mol%. At the optimum doping level, the ceramic exhibited the largest $P_r$ (15 $\mu$C/cm$^2$), $d_{33}$ (22 $\mu$C/N) and $p$ (129 $\mu$C/m$^2$K). Since the ceramics also have a relatively low $\varepsilon$ value (~99), their piezoelectric (voltage) coefficient (which is proportional to $d/\varepsilon$) and figure of merit for pyroelectricity (which is proportional to $p/\varepsilon$) are large and comparable to those of a lead-based ferroelectric ceramic. Together with the high Curie temperature, the BNTN ceramics therefore should be good candidates for various high-temperature sensing applications.

6.2 BNT Thin Films

$Bi_{3.3}Nd_{0.5}Ti_3O_{12}$ (BNT) thin films of thickness 900 nm have been successfully fabricated on platinized silicon substrates using a sol-gel method together with multiple-spin-coat technique. Our results reveal that the BNT thin films could crystallize well into a single phase of bismuth layered perovskite structure at 650°C and 700°C. However, a higher annealing temperature resulted in larger grains and better properties. The dielectric, ferroelectric as well as the piezoelectric and pyroelectric properties of the films were investigated. For the BNT thin film
annealed at 700°C, the observed $\varepsilon$, tan$\delta$, $P_r$, $p$ and $e_{31,f}$ (transverse piezoelectric coefficient) are 132, 0.034, 22 $\mu$C/cm$^2$, 148 $\mu$C/m$^2$K and 1.45 C/m$^2$, respectively. Similar to the cases for ceramics, owing to the low $\varepsilon$, the piezoelectric (voltage) coefficient and figure of merit for pyroelectricity of the films are large and comparable to those of a lead-based ferroelectric thin film. Therefore, the BNT thin films could be employed in various sensor applications.
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