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Microstructure development in temperature-stable BaTiO$_3$

Chiang, Shiuh-Kao, Ph.D.
The Ohio State University, 1989

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MICROSTRUCTURE DEVELOPMENT IN TEMPERATURE-STABLE BaTiO₃

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree of Philosophy in the Graduate School of the Ohio State University

by

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* * * * *

The Ohio State University

1989

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To My parents and My Family
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# TABLE OF CONTENTS

DEDICATION ..................................................... ii

ACKNOWLEDGMENT ............................................... iii

VITA ..................................................................... iv

LIST OF TABLES ................................................... ix

LIST OF FIGURES ................................................ x

ABSTRACT ........................................................ xvi

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. LITERATURE REVIEW</td>
<td>3</td>
</tr>
<tr>
<td>A. Historical Background</td>
<td>4</td>
</tr>
<tr>
<td>A. 1. Dielectric materials</td>
<td>4</td>
</tr>
<tr>
<td>A. 2. Barium titanate</td>
<td>5</td>
</tr>
<tr>
<td>B. Pure BaTiO$_3$</td>
<td>6</td>
</tr>
<tr>
<td>B. 1. Structure and dielectric behavior of single-crystal BaTiO$_3$</td>
<td>6</td>
</tr>
<tr>
<td>B. 2. Dielectric behavior of polycrystalline BaTiO$_3$ and the effect of grain size</td>
<td>10</td>
</tr>
<tr>
<td>C. Ferroelectric Domains in BaTiO$_3$</td>
<td>15</td>
</tr>
<tr>
<td>C. 1. Optical microscopy and scanning electron microscopy studies of ferroelectric domains in BaTiO$_3$</td>
<td>19</td>
</tr>
<tr>
<td>C. 2. Transmission electron microscopy study of the ferroelectric domains in BaTiO$_3$</td>
<td>20</td>
</tr>
</tbody>
</table>
D. Interpretation of Fringes in TEM Images ........ 24
E. Sintering of BaTiO₃ .................................. 27
   E. 1. Fast-fired BaTiO₃ .............................. 27
   E. 2. Non-stoichiometric sintering of BaTiO₃ .... 29
F. BaTiO₃ with Additives ............................... 30
   F. 1. Niobium doped barium titanate ............ 31
   F. 2. Bismuth doped barium titanate ............. 36
G. Temperature-Stable Dielectrics ..................... 38
   G. 1. Dielectric constant-temperature
         characteristics .................................. 38
   G. 2. Microstructural investigations ............. 43
   G. 3. The formation mechanism of the core-shell
         structure ......................................... 49
III. EXPERIMENTAL PROCEDURES .......................... 52
   A. Powder Processing ............................... 52
   B. Sintering ....................................... 60
   C. Density Determination ............................ 62
   D. X-ray Diffraction Analysis ...................... 62
   E. Thermal Analysis ................................ 64
   F. Dielectric Measurements ......................... 64
   G. Microstructural Examination ..................... 65
   H. Chemical Analysis ................................ 68
IV. RESULTS .............................................. 71
   A. Sintering ....................................... 71
      A. 1. Shrinkage .................................. 72
      A. 2. Density .................................... 77
      A. 3. Pore formation and swelling ............... 80
      A. 4. Weight loss ................................ 86
      A. 5. Reactions .................................. 92

B. Dielectric Properties ........................................ 103

B. 1. Samples with 0.05 mol dopants sintered at 1100°C ...................... 104
B. 2. Samples with 0.05 mol dopants sintered at 1150°C ...................... 106
B. 3. Samples with 0.03 mol dopants sintered at 1150°C ...................... 110

C. Microstructural Investigation ........................................ 113

C. 1. Bi2O3 and Nb2O5 doped BaTiO3 sintered at 1100°C ...................... 113
C. 2. Bi2O3 and Nb2O5 doped BaTiO3 sintered at 1150°C ...................... 119
C. 3. Bi2O3 doped BaTiO3 ............................................. 125

D. Grains with a Core-Shell Structure ................................... 132

D. 1. Grain core and grain shell ..................................... 132
D. 2. Planar defects in grain shell ................................... 139
D. 3. Chemical analysis ............................................... 146
D. 4. Ferroelectric to non-ferroelectric transformation ..................... 154

E. Grain Boundaries .................................................... 157

F. Nb- and Bi-Rich Phase .............................................. 166

F. 1. 1075°C air quenched sample ................................... 167
F. 2. 1100°C air quenched sample ................................... 172
F. 3. 1150°C 10 hrs. sintered sample ................................ 176

V. DISCUSSION ............................................................ 181

A. Sintering ............................................................. 181

A. 1. Effects of Bi2O3 and Nb2O5 .................................... 182
A. 2. Reactions during sintering ........................................ 188

B. Core-Shell Structure .................................................. 191

B. 1. Ferroelectric grain cores and non-ferroelectric grain shells .......... 192
B. 2. The core-shell structure formation mechanism ......................... 196
B. 3. Microstructure evolution and grain growth ............................ 201

vii
<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Average grain size of the Bi$_2$O$_3$ and Nb$_2$O$_5$ doped BaTiO$_3$ sintered at 1100°C</td>
<td>118</td>
</tr>
<tr>
<td>2. Average core and grain size of grains with core-shell structure in Bi$_2$O$_3$ and Nb$_2$O$_5$ doped BaTiO$_3$ sintered at 1100°C</td>
<td>118</td>
</tr>
<tr>
<td>3. Average grain size of 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped BaTiO$_3$ sintered at 1150°C</td>
<td>124</td>
</tr>
<tr>
<td>4. Average core and grain size of grains with core-shell structure in 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped BaTiO$_3$ sintered at 1150°C</td>
<td>124</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURES</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Diagram of the ideal perovskite lattice, showing one unit cell with the small quadrivalent ion in the center and its surrounding octahedron of the six oxygen ions [3]</td>
</tr>
<tr>
<td>2.</td>
<td>The structure of BaTiO$_3$. The unit cell is shown by the dotted line [17]</td>
</tr>
<tr>
<td>3.</td>
<td>Temperature variation of the lattice parameters of barium titanate, showing the various crystallographic transportations [20]</td>
</tr>
<tr>
<td>4.</td>
<td>The effect of temperature on the dielectric constant of a single crystal of BaTiO$_3$, along the c-axis and a-axis [24]</td>
</tr>
<tr>
<td>5.</td>
<td>Dielectric constant vs temperature of BaTiO$_3$ with various grain size [31]</td>
</tr>
<tr>
<td>6.</td>
<td>Straight lines mark 90° domain boundaries between a and c domains. Irregular round patches are 180° domain boundaries [50]</td>
</tr>
<tr>
<td>7.</td>
<td>(a) 90° a-a domain boundary, (b) 90° a-c boundary, (c) 180° a-a boundary and (d) 180° c-c boundary [62]</td>
</tr>
<tr>
<td>8.</td>
<td>Unconventional 90° domain boundary [62]</td>
</tr>
<tr>
<td>9.</td>
<td>90° a-a domain boundaries: (a) TEM BF image (Ca-doped), (b) schematic representation of domain boundary, (c) [100] diffraction pattern net and (d) [100] SADP [62]</td>
</tr>
<tr>
<td>10.</td>
<td>Temperature dependence of dielectric constant and of ceramic in the system (100-x) BaTiO$_3$+x NbO$_2$.5</td>
</tr>
</tbody>
</table>
11. Dielectric temperature characteristics of BaTiO$_3$-based X7R materials [119]. (I) BaTiO$_3$ + 0.03 mol "CdBi$_2$Nb$_2$O$_9"$ sintered for 4 hrs. at 1130°C; (II) BaTiO$_3$ + 0.03 mol Bi$_4$Ti$_3$O$_12$ sintered for 4 hrs. at 1110°C; and (III) X7R-3000 sintered for 3 hrs. at 1300°C. (IV) Dielectric temperature characteristics of hot-pressed fine-grained BaTiO$_3$ (average grain size 0.52 um) are shown for comparison ........................................ 40

12. Influence of cobalt oxide on the distribution of Nb (3.8 m/o) in barium titanate sintered at 1140°C 5 hrs. [117] ........................................ 42

13. Transmission electron micrograph of BaTiO$_3$ + 0.03 mol "CdBi$_2$Nb$_2$O$_9"$ sintered for 3 hrs. at 1200°C, showing the core-shell structure [119] ..................... 44

14. Schematic diagram of the unit cell transformation across the ferroelectric-paraelectric interface in BaTiO$_3$. Note the tetragonality is exaggerated by a factor of more than 400 for illustration purpose [63] .............................. 48

15. XRD of initial BaTiO$_3$ powder ........................................ 53

16. TEM images of BaTiO$_3$ powder ........................................ 54

17. SEM image of Nb$_2$O$_5$ powder ........................................ 55

18. SEM image of Bi$_2$O$_3$ powder ........................................ 55

19. XRD pattern of Nb$_2$O$_5$ powder ........................................ 57

20. XRD pattern of Bi$_2$O$_3$ powder ........................................ 58

21. Processing procedures ........................................ 59

22. Secondary electron SEM images of large BaTiO$_3$ particles ........................................ 61

23. Shrinkage behavior of BaTiO$_3$ with (a) 0.05 and (b) 0.03 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) ........................................ 73

24. Shrinkage behavior of (a) BaTiO$_3$ and (b) BaTiO$_3$+ 0.1 mol Nb$_2$O$_5$ ........................................ 74

25. Shrinkage behavior of BaTiO$_3$ with 0.1 mol Bi$_2$O$_3$ ....... 75
26. Comparison of the shrinkage behavior of BaTiO₃ with or without dopants ........................................ 76
27. Effect of composition and sintering time on density . 78
28. Effect of sintering temperature and time on density . 79
29. Effect of composition and sintering temperature on density for samples all fired 1 hr. .................. 79
30. Microstructure (near surface) of 0.05 mol doped samples sintered at 1150°C for (a) 1 and (b) 40 hrs. 82
31. Microstructure (interior) of 0.05 mol doped samples sintered at 1150°C for (a) 1 hr. and (b) 40 hrs. .... 83
32. Microstructure of 0.05 mol doped sample sintered for 1 hr. at 1250°C ........................................ 84
33. Microstructure of 0.1 mol Bi₂O₃ doped BaTiO₃ (a) near sample surfave and (b) in the interior ....... 85
34. TGA of Bi₂O₃ from (a) 100 to 1400°C and (b) 200 to 1150°C ..................................................... 87
35. TGA of (a) BaTiO₃ and (b) BaTiO₃+0.1 mol Nb₂O₅ ....... 88
36. TGA of BaTiO₃+0.1 mol Bi₂O₃ from (a) 200 to 1150 and (b) 100 to 1400°C ................................. 89
37. TGA of BaTiO₃ with 0.05 mol (Bi₂O₃+Nb₂O₅) from (a) 200 to 1150 and (b) 100 to 1400°C .......... 90
38. TGA of BaTiO₃ with 0.05 mol dopants heated at 1150°C for 10 hrs ........................................... 91
39. EDS spectrum from reacted layer .......................... 93
40. DTA of BaTiO₃ with 0.03 and 0.05 mol (Bi₂O₃+Nb₂O₅) .. 94
41. DTA of pure BaTiO₃ ...................................... 95
42. XRD of 0.05 mol Bi₂O₃ and Nb₂O₅ doped starting powder. Bi=Bi₂O₃, Nb=Nb₂O₅, BT=BaTiO₃ .......... 96
43. XRD of 0.05 mol doped sample heated and air quenched at 900°C ........................................... 96
44. XRD of (a) 1050 (b) 1075 and (c) 1100°C air quenched sample ....................................... 98

45. XRD of reaction product, BiNbO₄ ........................................ 99

46. XRD of (a) 0.03 mol doped and (b) 0.05 mol Bi and Nb doped samples .................................... 101

47. High-angle XRD of (a) pure BaTiO₃, (b) 0.03 mol doped and (c) 0.05 mol doped BaTiO₃ samples .......... 102

48. Dielectric property of 0.05 mol doped samples sintered at 1100°C ........................................... 105

49. Dielectric property of 0.05 mol doped samples sintered at 1150°C for 0.5 to 10 hrs. ......................... 107

50. Dielectric property of 0.05 mol doped samples sintered at 1150°C for 10 to 40 hrs. ......................... 108

51. Effect of sintering temperature on dielectric property ................................... 109

52. Dielectric property of 0.03 mol doped samples sintered at 1150°C ........................................... 111

53. Effect of composition on dielectric property ........... 112

54. Grains with a core-shell structure in 0.05 mol (Bi₂O₃ +Nb₂O₅) doped BaTiO₃ sintered at 1100°C for 1 hr. ... 114

55. Grains with a core-shell structure in 0.03 mol (Bi₂O₃ +Nb₂O₅) doped BaTiO₃ sintered at 1100°C for 2 hrs. ... 115

56. The core-shell structure in (a) small grains (arrowed) and (b) a large grain ............................... 117

57. Microstructures of 0.05 mol doped BaTiO₃ sintered at 1150°C for (a) 0.5 hr., (b) 2 hrs., (c) 4 hrs. and (d) 10 hrs. ........................................... 120

58. Microstructures of 0.05 mol doped BaTiO₃ sintered at 1150°C for (a) 20 hrs. and (b) 40 hrs. ............... 121

59. Microstructures of 0.1 mol Bi₂O₃ doped BaTiO₃ sintered at 1150°C for (a) 1 hr. and (b) 40 hrs. .... 126
60. Microstructures of (a) 0.1 mol Bi$_2$O$_3$ and (b) 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped BaTiO$_3$ sintered at 1150°C for 40 hrs. ........................................ 127

61. Second phase (arrowed) in 0.1 mol Bi$_2$O$_3$ doped BaTiO$_3$ sintered at 1150°C for (a) 1 hr. and (b) 40 hrs. ........................................ 129

62. TEM (a) BF image, (b) diffraction pattern and (c) EDS spectrum of the second phase in 0.1 mol Bi$_2$O$_3$ doped BaTiO$_3$ sintered at 1150°C for 40 hrs. ......................... 130

63. EDS spectra of a 2nd phase, the grain boundary (G.B) and inside a grain (GR). TEM image showing the analyzed area ..................................................... 131

64. TEM BF image of a grain with a core-shell structure. This specimen was doped with 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) and sintered at 1150°C for 2 hrs. ......................... 133

65. TEM BF image of a grain with a core-shell structure. This specimen was doped with 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) and sintered at 1150°C for 0.5 hr. ....................... 134

66. TEM DF images (g=011) of a grain examined at (a) 30°C and (b) 132°C. This specimen was doped with 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) and sintered at 1150°C for 0.5 hr. .... 136

67. TEM electron diffraction patterns of (a) the grain core and (b) the grain shell. Note the splitting of spots (arrowed) in (a) but not in (b) ............... 138

68. Planar defects in the grain shell ........................................ 141

69. TEM (a) BF image and (b) diffraction pattern of a grain with three set of planar defects (A, B and C) in the shell ........................................ 142

70. TEM DF images of a grain with three sets of planar defects (A, B and C) when (a) g=10$ar{1}$, (b) g=01$ar{1}$ and (c) g=1$ar{1}$0 ........................................... 143

71. TEM DF image of a grain (g=11$ar{1}$) showing one of the planar defects in the shell perpendicular to <111> ... 144

72. TEM (a) BF and (b) DF images of the planar defects in the shell ........................................ 145

xiv
EDS spectra of (a) the grain core and (b) the grain shell ........................................ 147

Bi and Nb concentration profiles across a grain sintered at 1150°C for 0.5 hr. ..................... 148

Bi and Nb concentration profiles across a grain sintered at 1150°C for 4 hrs. .......................... 150

Bi and Nb concentration profiles across a grain sintered at 1150°C for 10 hrs. ......................... 151

Bi and Nb concentration profiles across grains sintered at 1150°C for (a) 0.5 hr., (b) 4 hrs. and (c) 10 hrs. 152

TEM BF images of a grain sintered at 1150°C for 4 hrs. and examined at temperatures from -174°C to 140°C .. 155

TEM BF images of a grain sintered at 1150°C for 10 hrs. and examined at temperatures from -174°C to 140°C (grain core is arrowed) .................................................. 156

Dislocations on grain boundaries of specimens sintered at 1150°C for (a) 0.5 hr. and (b) 2 hrs. ......... 158

Dislocations on grain boundaries of specimens sintered at 1150°C for (a) 10 hrs. and (b) 40 hrs. .......... 159

Boundary ledges on grain boundaries of specimen sintered at 1150°C for (a) 4 hrs., (b) 4 hrs. and (c) 10 hrs. .......... 160

Bi and Nb concentration profiles across a grain boundary of the sample sintered at 1150°C for 0.5 hr. 162

Bi and Nb concentration profiles across a grain boundary of the sample sintered at 1150°C for 10 hrs. 163

Bi and Nb concentration profiles across the boundaries of samples sintered at 1150°C for 0.5 and 10 hrs. .................................................. 164

TEM images of (a) ferroelectric grains and (b) non-ferroelectric grains in 1075 °C air quenched and 0.05 mol (Bi2O3+Nb2O5) doped BaTiO3 ........................................ 168

TEM image and EDS spectrum of Nb and Bi-rich phase in 1075°C air quenched sample .................... 169
88. TEM image and EDS spectra of grains with different compositions in the 1075°C air quenched sample
89. TEM (a) DF image and (b) diffraction pattern of a Nb- and Bi-rich phase
90. Microstructures of 1100°C air quenched and 0.05 mol (Bi₂O₃+Nb₂O₅) doped BaTiO₃
91. TEM image and EDS spectra of grains with different compositions in 1100°C air quenched sample
92. EDS spectra of grain cores (1 and 4), grain shells (2 and 5) and grain boundaries (3 and 6) in 1100°C air quenched sample
93. TEM image and EDS spectra of grains with different compositions in 1150°C 10 hrs. sintered sample
94. Microstructure of grain with different compositions in 1150°C 10 hrs. sintered sample
95. EDS spectra of the Nb and Bi-rich phase in (a) 1075°C air quenched and (b) 1150°C 10 hrs sintered samples
96. Proposed mechanism for the transport of dopants and microstructure evolution
97. A schematic representation of grain growth and the elimination of small grains
98. Dielectric constant of grain core (assume two-phase mixture model)
99. Dielectric constant of grain shell (assume two-phase mixture model)
100. Dielectric behavior of transition zone
101. A schematic representation of the dielectric behavior of the shell, the core and the transition zone
Temperature-stable dielectric materials with high dielectric constants are widely utilized for manufacturing multilayer ceramic capacitors. Ferroelectric barium titanate is usually doped with different additives for this purpose and the temperature dependence of the permittivity is determined by the degree of chemical heterogeneity in the doped material.

In a number of temperature-stable dielectrics, a core-shell structure has been observed. The grain core, containing ferroelectric domains, consists of relatively pure BaTiO₃. The grain shell, on the other hand, is non-ferroelectric at room temperature and contains all of the dopants.

BaTiO₃ doped with 0.03 or 0.05 mol (Bi₂O₃+Nb₂O₅) was sintered at 1100 or 1150°C for 0.5 to 40 hrs. The core-shell structure was observed by transmission electron microscopy in the sintered
microstructure. The ferroelectric nature of the grain core was clearly demonstrated by the presence of domain fringes. The grain shell was non-ferroelectric but contained planar defects which are most likely stacking faults. The ferroelectric domains in the grain core were confirmed by splitting of electron diffraction spots. Electron diffraction reflections from the non-ferroelectric shell, however, showed no splitting.

EDS (Energy Dispersive Spectroscopy) microanalysis demonstrated that Bi and Nb were enriched in the grain shell and the amount of dopants gradually decreased toward the core center. Longer sintering times resulted in a reduction of core size and an increase of dopant content in the core. Microstructural and microchemical investigation revealed that the distribution and the concentration of dopants varied with sintering time and temperature. The transport and distribution of the dopants were conducted by diffusion and grain growth. A Nb-and Bi-rich phase acted as the dopant source to supply Nb ana Bi during sintering.

Ferroelectric BaTiO₃ gradually transformed into the non-ferroelectric state with increasing concentration of dopants. The ferroelectric transformation temperature decreased with increasing dopant content. The dielectric temperature-stability of material with the core-shell structure actually contains contributions from three distinct regions, i.e. the dopant-containing solid solution
shell, pure BaTiO$_3$ core, and the transition zone. The transition zone is composed of regions with different dopant contents and underwent non-ferroelectric to ferroelectric transformation continuously from -174°C to 130°C.
Temperature-stable dielectric materials with high dielectric constants are widely utilized for manufacturing multilayer ceramic capacitors. The basic function of a capacitor is energy storage. Small multilayer capacitors are physically compatible with solid-state semiconductor components and are usually used in hybrid circuitry. For this purpose, the dielectric temperature-stability of the capacitor is very important since the circuits are expected to function in a variety of ambient conditions and heat output from the semiconductor components can be high. To achieve temperature stability ferroelectric barium titanate is usually doped and the temperature dependence of the permittivity is determined by the degree of chemical heterogeneity in the doped material.

In a number of temperature-stable dielectrics, a core-shell structure has been observed. The grain core, containing ferroelectric domains, consists of relatively pure BaTiO$_3$. The grain shell, on the other hand, is non-ferroelectric at room temperature and contains most of the dopants. The temperature-stable dielectric behavior from such a chemically inhomogeneous system has been explained by the superimposition of two separate dielectric-
temperature curves, one from the relatively pure grain core
(Tc=120°C) and the other from the dopant-containing shell which
shows a permittivity maximum at room or even lower temperature.

The dielectric behavior of temperature-stable dielectrics has
been explained qualitatively. However, a detailed correlation
between the microstructure and dielectric properties is lacking.
Furthermore, the formation mechanism of the core-shell structure
and the effects of dopants on the structural change and the
dielectric behavior of BaTiO₃ have not been explained. In this
study, detailed microstructural and chemical analyses were performed
on doped BaTiO₃ with an Analytical Electron Microscope (AEM). From
these results, a correlation was made between the observed
microstructure, dopant distribution and the dielectric properties.

Bi₂O₃ and Nb₂O₅ were chosen for this study because they are
commonly used as dopants in BaTiO₃ and were known to promote
temperature stability.
CHAPTER II
LITERATURE REVIEW

Barium titanate, because of its exceptionally high dielectric constant, $k' = 1000-5000$, is used extensively in ceramic multilayer capacitors. The permittivity of barium titanate, however, shows marked changes with temperature which is related to the ferroelectric transitions. For many applications, the temperature dependence of the dielectric constant of pure BaTiO$_3$ is much too high. As a result, there have been many studies on the effect of additives such as Nb or Zr or the solid solution, e.g. mixing BaTiO$_3$ with SrTiO$_3$, on properties. It has been found that the dielectric properties of BaTiO$_3$ are strongly dependent on dopant concentration, heat treatment, sintering atmosphere and the final microstructure.

In this chapter, the historical background of capacitor materials and barium titanate are introduced. Previous studies on single-crystal or polycrystalline BaTiO$_3$ and the ferroelectric domains in BaTiO$_3$ are also surveyed. In addition, sintering of BaTiO$_3$, the effects of additives and temperature-stable BaTiO$_3$-based dielectrics are reviewed.
A. Historical Background

The capacitor is a fundamental electrical device capable of storing electrical energy. It was discovered by E. G. von Kleist in 1745 and, independently, by P. van Musschenbroek of the University of Leyden at about the same time [1]. The first capacitor, which came to be known as the Leyden jar, consisted of a stoppered glass vial or jar filled with water. The glass served as the dielectric material. Another fundamental step in the evolution of the capacitor was taken by John Bevis in 1746 [1] when he replaced water with metal foil as the electrodes. This form of the capacitor, with two metal electrodes insulated from each other by a dielectric material, has been retained in every modern form of capacitor.

The capacitance depends not only on the geometrical area and thickness of the dielectric material, but also on the type of the material used. In fact, the properties of the dielectric material are at the heart of the capacitor and have been the subject of much scientific and engineering investigation in the past.

A. 1. Dielectric materials

The properties of dielectric materials which determine the functions of a capacitor include: (1) the dielectric constant relative to that of vacuum, commonly known as the relative dielectric constant, $k'$, or permittivity; (2) the dissipation factor, $\tan \delta$; (3) the insulation resistance; and (4) the
temperature, frequency and field strength dependencies.

Electrical porcelain was a major dielectric material for capacitors and persisted in use into the twentieth century [2]. Steatite ceramics, containing feldspar as a fluxing constituent, were then developed for the same application [2]. In the early twentieth century, the major dielectric materials for the capacitors in the first radio circuitry were paper and mica [2]. Besides having good loss characteristics, these materials could be fabricated in thin sheets to provide high capacitance in spite of their modest dielectric constant. The dielectric constant, k', of mica is 5.4 and k' of Kraft paper is 2.2 [1]. Owing to material shortages (especially of condenser grade mica) in World War II, extensive investigations were conducted to develop a substitute for mica [3].

A. 2. Barium titanate

In about 1940, the Titanium Alloy Manufacturing Company, in an attempt to develop new uses for titanium dioxide, started a program of research into ceramics containing TiO$_2$. As a result of this work, carried on by Wainer and co-workers, barium titanate with extremely high dielectric constant was discovered in 1942 [4]. Simultaneously, independent work was being carried out in the United States [5-7], Japan [8], Russia [9-11] and England [12-15], and these results were reported right after the war.
As a result of the wartime work, barium titanate was found to be a ferroelectric material with extremely high dielectric constant. Since the discovery of barium titanate, a host of combinations of titanate ceramic dielectrics have been discovered and applied in the dielectric industry.

B. Pure BaTiO$_3$

The discovery of ferroelectric barium titanate during World War II initiated a new era of ceramic dielectrics. Because of its extremely high dielectric constant, BaTiO$_3$ has become the most widely used ceramic capacitor material and has been studied extensively. Previous studies on the crystal structure, and the dielectric properties of single crystal and polycrystalline BaTiO$_3$ are reviewed in this section.

B. 1. Structure and dielectric behavior of single-crystal BaTiO$_3$

Barium titanate has a crystal structure of the perovskite type (named for the mineral perovskite CaTiO$_3$) [16]. This structure can be thought of as a cubic close packing of barium and oxygen ions, where barium ions are located at the corners of the unit cell and oxygens at the face centers, as shown in Fig. 1 [3]. Octahedrally-coordinated titanium ions located in the center of the perovskite cell are the active ions in promoting ferroelectricity. Alternatively, this structure can be thought as a network of TiO$_6$
octahedral linked by their corners, with barium ions being accommodated in the large central hole between the octahedra, as shown in Fig. 2 [17].

The structure of BaTiO$_3$ has been extensively studied by several investigators [17-23]. Barium titanate has the ideal cubic structure above 120°C up to 1327°C [19], but on cooling below this temperature three reversible ferroelectric transitions occur, Fig. 3 [20]. At the Curie temperature, T$_c$ (120°C), the oxygen and titanium ions shift relative to the barium ions and the cubic unit cell transforms into the ferroelectric tetragonal structure with one axis (called the "c" axis) about one percent longer than the other two [17-18]. At about 0°C there is a further shift of the ions and the symmetry of the crystal becomes orthorhombic [20-22]. On further cooling, a third transition takes place at -90°C and the unit cell transforms into rhombohedral symmetry [20].

The dielectric constant-temperature plot of single-crystal BaTiO$_3$ displays three maxima, as shown in Fig. 4, which can be attributed to these three reversible ferroelectric transitions [24]. When the BaTiO$_3$ crystal transforms from the cubic to tetragonal form, the ionic shifts in the unit cell cause a dipole moment in the crystal. The resulting spontaneous polarization along the [001] direction gives a peak for the dielectric constant at the Curie point (120°C). This polarization changes to the [011] and to the
Fig. 1 Diagram of the ideal perovskite lattice, showing one unit cell with the small quadrivalent ion in the center and its surrounding octahedron of the six oxygen ions [3].

Fig. 2. The structure of BaTiO₃. The unit cell is shown by the dotted line [17].
Fig. 3. Temperature variation of the lattice parameters of barium titanate, showing the various crystallographic transportation [20].

Fig. 4. The effect of temperature on the dielectric constant of a single crystal of BaTiO$_3$, along the c-axis and a-axis [24].
[111] direction at lower temperatures giving rise to the other two peaks in the dielectric constant.

B. 2. Dielectric behavior of polycrystalline BaTiO$_3$ and the effect of grain size

The temperature characteristic of polycrystalline BaTiO$_3$ has the same features as a single crystal. A sharp dielectric constant maximum occurs at about 120°C and lesser maxima at the other crystallographic transitions [25-32]. It has been found, however, that the dielectric properties of polycrystalline BaTiO$_3$ have a strong grain size dependence [25-32]. Although there is not complete agreement among previous workers, the general consensus is that when the average grain size is small (around 1 um) the dielectric constant of the tetragonal phase is raised. On the other hand, in the orthorhombic and rhombohedral phases, k' of fine-grained ceramics was not always higher than that of coarse-grained ceramics [30].

For polycrystalline BaTiO$_3$, coarse-grained (>10 um) ceramics have a relative dielectric constant, k', around 1500 to 2000 in the temperature range 20-80°C. Higher values of k' (3500-5000), however, are observed in the same temperature range in dense, fine-grained (around 1 um), BaTiO$_3$, as shown in Fig. 5 [31]. The highest values of k' (5000-6000) for this temperature range were observed when the
Fig. 5. Dielectric constant vs temperature of BaTiO$_3$ with various grain sizes [31].
average grain size is 0.7-0.8 μm [31]. At sizes <0.5 μm the permittivity is rather low again, about 2500, [31 and 32]. As shown in Fig. 5, a temperature-stable dielectric constant curve was observed by Arlt, et al. [31] when the average grain size was 0.28 μm and the main impurity was 0.05 wt% Al₂O₃. However, this temperature-stable behavior in the hot-pressed and very fine-grained BaTiO₃ (0.28 μm) was not explained by the authors.

At the grain size around 1 μm, the reported Curie temperature and the maximum dielectric constant value at the Curie peak were not consistent [30, 31]. A sharp and high dielectric constant peak at 120°C was observed by Kinoshita and Yamaji [30] in hot-pressed and fine-grained BaTiO₃ (1.1 μm). In contrast, Arlt, et al. found that at the grain sizes of 0.7 μm, the Curie peak moved upward to around 140°C and the dielectric constant maximum value was suppressed. It is believed that the observed scatter of the dielectric behavior near the Curie temperature is caused by the preparation parameters, such as sintering, impurities, Ba/Ti ratio and the atmosphere.

The physical reasons for the maximum room temperature permittivity at grain sizes of 0.7-0.8 μm are not completely understood. At room temperature, the dielectric constant of BaTiO₃ single crystal is strongly anisotropic with k' = 4000 along the a axis and k' = 200 along the c axis [24]. In sintered polycrystalline BaTiO₃, where the grains are randomly oriented and the contribution
from $90^\circ$ domains is neglected, the average calculated value of $k'$ was 940-1200 (depending on the electric field) [33]. The calculated result cannot, therefore, explain the measured $k'$ values in coarse-grained and especially the fine-grained polycrystalline BaTiO$_3$ ceramics. The observation of grain size dependence of the permittivity, however, illustrates the importance of controlling the grain size in materials to be used in practical applications.

Buessem, et al. [34,35] interpreted the higher values of $k'$ in fine-grained BaTiO$_3$ as being due to the effect of internal stress in the grains, and their interpretation was based on Little's [36] measurement of the domain wall thickness. Little had measured the thickness of the $90^\circ$ domain wall using a polarizing optical microscope and obtained a value of about 0.4 μm. Buessem, et al. thus suggested that it was impossible to have a domain wall in a 1 μm grain. Since domains relieve the strains generated during the cubic to tetragonal transformation, large internal stresses would occur in fine grains (<1 μm) when domain formation is inhibited. Therefore, they assumed that grains smaller than 1 μm would be single-domain grains, containing no $90^\circ$ domains. Using the Devonshire phenomenological thermodynamic method [123], Buessem, et al. [34, 35] showed that the internal stress should give rise to an increase of permittivity in fine-grained BaTiO$_3$.

Arlt, et al. [31], on the other hand, interpreted the higher permittivities of BaTiO$_3$ ceramics in terms of domain wall
contributions. The permittivity of BaTiO₃ ceramics can be regarded as the sum of a volume contribution, which is based on the single-crystal dielectric constants, and a contribution from the ferroelectric domain walls moving in the electric field, i.e. \( k'(T) = k'_{\text{vol}}(T) + k'_{\text{dom}}(T) \). The contribution of the 90° domain walls to the real part of the dielectric constant is proportional to the total area of 90° domain walls per unit volume, i.e. \( k'_{\text{dom}} = k A_{\text{dom}} \), where \( k \) is a constant and \( A_{\text{dom}} \) is the total area of domain per unit volume. Arlt, et al. [31] observed domains in grains less than 1 μm, and found the distance between domain boundaries decreased with grain size, and the total area of domain wall increased. They, therefore, attributed the increase of \( k' \) in fine-grained BaTiO₃ to the domain boundary contribution.

As described above at least two different interpretations have been proposed to explain the grain size effect on the dielectric properties of polycrystalline BaTiO₃ ceramics. The major difference between them, however, comes from the assumption of the existence of domains in small BaTiO₃ grains. The microstructural support of Buessem, et al.'s assumption was the domain wall thickness measurement using a polarizing optical microscope [36]. On the other hand, Arlt, et al. observed domains in small grains (<1 μm) using a TEM [31]. The higher resolution of the TEM means that the microstructural observations made with it are likely to be more reliable than those made with an optical microscope.
C. Ferroelectric Domains in BaTiO₃

Barium titanate has the cubic perovskite structure above the Curie Temperature, Tc= 120°C. Upon cooling below 120°C the basic lattice of barium titanate is slightly distorted to form a tetragonal phase in which c/a=1.01 at the room temperature [17]. This transformation is accompanied by the formation of ferroelectric domains, and these domains in BaTiO₃ have been studied in detail by numerous investigators [31, 37-66]. In an individual domain, the direction of spontaneous polarization occurs along the elongated c axis, i.e. [001] direction. This polarization direction is parallel to any one of the three original <001> cube axes.

Two types of domain boundaries, 90°, and 180°, have been observed in tetragonal BaTiO₃ [31, 37-66], and the angles refer to the angle between the domain polarization vectors on either side of the boundary. The angles between the c axes in adjacent domains are actually 89°25' and 180°. The terminology "90° domain," is generally accepted and refers to the nearly 90° direction of polarization difference in adjacent domains. 90° domains were commonly observed in tetragonal BaTiO₃ in the early studies [37-43]. The 180° domain boundaries, on the other hand, were first discovered by Merz in 1952 [44] when an electric dc field was applied. The 90° boundary walls have been found to lie on (110) planes and tend to be straight [31, 37-56, 58-64]. In addition, the polarization vectors adopt a "head-
to-tail" arrangement across a 90° boundary in order to minimize the charge at the domain wall. The energy of 180° boundary walls, however, is less sensitive to crystallographic orientation; thus 180° boundaries are usually "wavy" [50-51, 56-57, 62]. The straight 90° domain boundaries and the irregular rounded 180° boundaries are shown in Fig. 6, taken from reference 50.

Much of the nomenclature in domain studies derives from early work carried out on Remeika [67] single crystals using a polarizing optical microscope with the plane of the crystal as the (001) plane and the crystal edges lying along the [100] and [010] directions. Domains are designated as either "a" or "c" domains. While viewing down on the (001) planes, the c domain is oriented so that the c axis of the unit cell is parallel to the viewing direction. The a domain is when the c axis of the unit cell is perpendicular to the viewing direction. The resulting nomenclature for the observed domain boundaries can be classified into 4 types: (1) 90° a-a boundaries, (2) 90° a-c boundaries, (3) 180° a-a boundaries and (4) 180° c-c boundaries. These four types of boundary are shown schematically in Fig. 7 [62]. However, it should be noted that the (1) and (2) types boundaries are structurally identical, as are type (3) and (4), the only difference between them being the viewing direction. In a recent study of the domain boundaries, Hu, et al. [62] found unconventional 90° domain boundaries and a schematic representation of this unconventional boundary is shown in Fig. 8.
Fig. 6. Straight lines mark $90^\circ$ domain boundaries between a and c domains. Irregular round patches are $180^\circ$ domain boundaries. (x 250)
Fig. 7. (a) 90° a-a domain boundary, (b) 90° a-c boundary, (c) 180° a-a boundary and (d) 180° c-c boundary [62].

Fig. 8. Unconventional 90° domain boundary [62].
C. 1. Optical microscopy and scanning electron microscopy studies of ferroelectric domains in BaTiO$_3$

Optical microscopy was generally used in early studies of ferroelectric domains in BaTiO$_3$ [31, 36-51]. Due to the strain birefringence and the difference in refractive indices along the a and c axes, transmitted polarized light was able to reveal the 90° domain boundaries in BaTiO$_3$ [36-43]. Under normal viewing conditions, the optical microscope is unable to discern 180° domain boundaries. However, when an electric field is applied perpendicular to the samples surfaces, the 180° boundaries become visible in polarized light because of the increased internal strain and the opposite polarization directions in two adjacent antiparallel domains [44-45].

As well as in the polarizing optical microscope, BaTiO$_3$ domains were also observed using the reflecting optical microscope after chemical etching [46-51]. BaTiO$_3$ domains can be revealed on the surface by chemical etching because the different orientations etch at different rates, so the surface topography contrast can be observed. Using chemical etching, both 90° and 180° domain boundaries could be observed [46, 50-51]. Scanning electron microscopy was also applied to study the domains in BaTiO$_3$ [31, 52-53, 62]. The topographic contrast on the etched surface was used to study the domain configurations. Similar to optical microscopy, both 90° and 180° domain boundaries were detected [62].
Using the polarizing optical microscope, Little [36] measured the 90° domain wall thickness as 0.4 um. Based on this observation, Buessem then assumed that fine BaTiO₃ grains (<1 um) were all monodomain. However, SEM and TEM revealed that domains were still present in BaTiO₃ grains of sizes small than 1 um [31]. Owing to the limited magnification and resolution of the optical microscope, Little's observation evidently misled Buessem.


Ferroelectric domain boundaries can be revealed in the TEM by diffraction contrast in images [54-64] or by spot splitting in electron diffraction patterns [56, 61-64]. Boundaries inclined with respect to the foil plane produce fringe patterns which look similar to those in stacking faults or thickness fringes. Gevers and his co-workers [58-60] have applied the dynamical theory of image contrast to calculate the image characteristics of 90° domain boundaries in BaTiO₃, and they were able to confirm the results of their calculations by studying the fringe contrast of inclined domain walls at carefully chosen imaging conditions. For BaTiO₃ 90° domain boundaries (an example of a δ boundary), the nature of the first and last fringes is asymmetrical in bright-field (BF) image, and it is symmetrical in the dark-field (DF) image. Analysis of the type of domain boundary 90° or 180° by fringe contrast requires complicated
tilting and imaging experiments, but the appearance of fringes can clearly illustrate the existence of ferroelectric domains.

To analyze the domain wall type in BaTiO₃, Shakmanov and Spivak adopted another approach [61]. They calculated the selected-area diffraction patterns (SADP) which would be produced for simple domain configurations. When part of the electron beam passes through one domain and part through a second domain, the electron diffraction pattern will represent the superposed diffraction patterns from each of the domains. Due to the orientation difference between domains, the diffraction spots in the pattern will be split. By observing the splitting of the high-order diffracted spots, the domain wall type can then be determined [61, 62]. An example showing the TEM image, schematic domain boundary and diffraction pattern of a 90° a-a domain boundary is illustrated in Fig. 9. Consequently, selected-area diffraction patterns as well as fringe contrast can be used to determine the existence of ferroelectric domains in BaTiO₃.

In previous studies, TEM was applied to examine the existence of domains in fine-grained (<1 um) BaTiO₃ [31, 65-66]. In a TEM study of replica etched surfaces in Dy-doped fine-grained BaTiO₃, Yamaji, et al. [65] and Enomoto and Yamaji [66] found a decrease in the number of 90° domains with decreasing grain sizes. At grain sizes below 0.75 um, no domains were observed. In contrast, Arlt, et al. [31] studied ion thinned specimens in a TEM, and found domain
fringes in grains smaller than 1 um but larger than 0.4 um. Moreover, they found the distance between 90° domain walls decreased with the grain size. The observation discrepancy is believed to be a result of the experimental technique. Chemical etching of 90° domains in fine-grained ceramics generally leads to problems. Owing to the higher etching rate in grain boundaries compared to 90° domain boundaries, small grains (about 1um) are often completely eliminated before the 90° domains begin to etch [31]. The results obtained from ion thinned TEM specimens are thus more reliable. In addition, TEM domain boundary fringes and the selected-area diffraction pattern are the most powerful experimental technique to illustrate the existence of ferroelectric domains in fine-grained BaTiO₃.
Fig. 9. 90° a-a domain boundaries (a) TEM BF image (Ca-doped) (b) schematic representation of domain boundary, (c) [100] diffraction pattern net and (d) [100] SADP [62].
D. Interpretation of Fringes in TEM images

Planar defects produce fringes if they lie on an inclined plane running from the top to the bottom of the TEM specimen. Many planar defects are found in crystalline materials including domain (δ) boundaries, stacking faults or planar precipitates (α boundaries) and antiphase domain boundaries (π boundaries). These defects cause a change in phase of an incoming electron wave in the TEM. The extent of the change in phase is described by a phase factor, \( a = 2\pi g \cdot R \), where \( g \) is a reciprocal lattice vector and \( R \) a displacement vector associated with the boundary. In the case of \( a = \pi \), the specific planar defect is an antiphase domain boundary.

The contrast arising from stacking faults has been studied theoretically for f.c.c. metals by Whelan and Hirsch [68, 69], Hirsch, et al. [70] and Gevers, et al. [71-72]. The diffraction contrast fringes of a stacking fault in the BF image consist of a series of alternate dark and bright lines. These fringes are parallel to the intersection of the fault planes and the foil surface. Furthermore, the outer fringes in BF are both dark or bright, so the image is termed symmetric. The DF image of a stacking fault is also a series of fringes but the outer fringes are not the same, the image is termed asymmetric. A precipitate plane is another kind of \( \alpha \) boundary. If the precipitate does not contribute to the diffraction process then \( \alpha \) fringes will occur with symmetric BF and asymmetric DF images like stacking faults.
Antiphase phase boundaries (APB) (π boundaries) are a special case of a boundaries with $a - \pi$ and have specific image characteristics. This planar defect is usually observed in ordered materials and occurs when there is a change in the identity of the atom at a given lattice point but there is no atomic stacking change like that at a stacking fault. Diffraction contrast imaging of an antiphase phase boundary has been treated theoretically by several investigators [73-74]. APB images only occur for excitation of reflections for which $a - \pi$, that is, in general for superlattice, not fundamental, reflections. The image of a π boundary or APB consists of alternate black/white fringes parallel to the intersections of the habit plane with the foil surface. Both BF and DF images are symmetric about a foil center. In addition, over the whole depth of the foil BF and DF images have exactly opposite contrast.

Twin boundaries will also cause diffraction contrast fringes in TEM images. Since a twin is simply one part of the crystal oriented with respect to another according to a symmetry rule, extra diffraction spots arise in the selected-area diffraction pattern. Therefore, it is easy to distinguish twin boundaries from the other planar defects by analyzing the diffraction pattern. In BaTiO₃, twin boundaries along (111) habit planes have been observed in the optical microscope [50, 75-76] and TEM studies [76, 77].
Ferroelectric domains have been described as twins by many authors particularly in the early studies [21, 36-38, 42]. In a TEM study of the BaTiO$_3$ twin boundaries extra diffraction spots were clearly observed and attributed to the superposition of the matrix and twinned area [77].

In addition to these boundaries or planar defects, wedge-shaped and elastically bent TEM foils will also exhibit fringes in images. These fringes, however, are usually not straight and not limited to a single grain. Therefore, the appearance of thickness fringes and bend extinction contours can be easily recognized.
E. Sintering of BaTiO$_3$

The properties of ceramic components are decisively influenced by the sintering treatment. For instance, at room temperature the dielectric constant of a polycrystalline BaTiO$_3$ can be increased to 3500-5000, if the average grain size is around 1 um [25-32]. The dielectric properties and temperature characteristics of multilayer capacitors are also greatly affected by the final microstructure and the distribution of dopants. Consequently, the sintering treatment of BaTiO$_3$ is crucial in determining the properties of polycrystalline BaTiO$_3$ ceramics.

E. 1. Fast-fired BaTiO$_3$

To achieve small grain sizes in fired BaTiO$_3$ ceramics, it has been common to use additives as grain growth inhibitors (see section F). An alternative method is to control the processes responsible for the rates of densification and grain growth by controlling the sintering parameters, time and temperature. When the processing conditions are controlled so that densification is enhanced and grain growth is suppressed, high density and small grain size ceramics are then obtained.

During firing, densification and grain growth involve different atomic transportation mechanisms. Both the densification rate, $d$, and the grain growth rate, $g$, are hence exponentially dependent on temperature by equations of the form [79]:
Where \( H_d \) and \( H_g \) are the enthalpies associated with the densification rate, \( \dot{d} \), and the grain growth rate, \( \dot{g} \), respectively. Short, high-temperature firings will be beneficial to densification if \( H_d > H_g \) \[76\]. Furthermore, by spending as short a time as possible in the low temperature region, the pronounced grain coarsening process that occurs at low temperature will also be suppressed.

Mostaghaci and Brook \[78-80\] found that fast-firing, which involves a short high temperature firing treatment (5 min at 1450\(^\circ\)C), could sinter barium titanate to a high-density (95\%) with small grain sizes (about 5\,\mu m). Excess BaO decreased the densification rate, but led to a finer grain size. With 8 mol\% excess BaO, the fast-fired sample (1450\(^\circ\)C 5 min) had a density less than 5.45 g/cm\(^3\) (91\%) \[78\]. The firing temperature was important in determining the structure of the sintered material \[78\]. The tetragonal phase was identified in almost all the samples fired at temperatures up to 1450\(^\circ\)C. At temperatures higher than 1450\(^\circ\)C, the hexagonal phase of BaTiO\(_3\) was a predominant feature. Mostaghaci and Brook also showed that \[80\], through the same process the highest density was obtained with a powder of relative narrow size distribution and fine size.
The results of the fast-firing method showed enhanced densification relative to grain growth. This observation then implies the activation enthalpy of the densification mechanism, $H_d$, (lattice or grain boundary diffusion) is higher than the enthalpy of the mechanism responsible for grain growth process, $H_g$ (possibly surface diffusion) \[79\]; and high density, fine-grained BaTiO$_3$ ceramics with high dielectric constant at room temperature could be obtained.

E. 2. Non-stoichiometric sintering of BaTiO$_3$

The melting point of BaTiO$_3$ is 1612°C, and pure dense BaTiO$_3$ ceramics can only be achieved after sintering above 1400°C [48-50]. BaTiO$_3$ materials are normally sintered to high density with small excess TiO$_2$ (0.5-3 mol%) as the sintering aid [27, 31, 82-83]. TiO$_2$ is thought to react with BaTiO$_3$ to form Ba$_6$Ti$_{17}$O$_{40}$ which forms a eutectic with BaTiO$_3$ at 1312°C [81]. The liquid phase is generally believed to promote densification and give rise to pronounced discontinuous grain growth [82-83].

Schmelz and co-workers [84-86] studied pure BaTiO$_3$ sintered with 3 mol% excess TiO$_2$ at 1240°C to 1340°C. They observed anomalous grain growth below the eutectic temperature. Typically twin lamellae formed in the large grains [85]. At temperatures exceeding the eutectic temperature, they also found anomalous grain
growth in BaTiO$_3$ ceramics was accompanied by twin formation [84]. Consequently, they concluded that anomalous grain growth was initiated by a twinning process and was not dependent on the presence of liquid phase. It is difficult to evaluate the feasibility of the initiation of anomalous grain growth by twin formation even though abnormal grain growth has often been observed with the presence of liquid phase [82-83, 87]. However, Schmelz, et al. [84-86] also showed strong experimental evidence linking the anomalous grain growth and twinning.

F. BaTiO$_3$ with Additives

High-permittivity dielectric ceramic materials are usually based on ferroelectric barium titanate. Owing to the inferior temperature stability of pure BaTiO$_3$, suitable temperature coefficients and high dielectric constants are only possible by making compositional changes. By incorporation of so-called "peak-shifters", like Sr for Ba [88] and Zr or Sn for Ti [89-91], the Curie temperature can be reduced to room temperature with a high and broad permittivity maximum.

A disadvantage of these materials, however, is the high sintering temperatures and extended sintering times required. Manufacturing costs would be considerably lowered if materials could be found which sinter fast at low temperatures, but have the same dielectric properties [92-95]. Low-sintering dielectric materials
would also be useful in the manufacture of multilayer capacitors, enabling the very expensive Pd electrodes to be replaced by the much cheaper and lower melting electrodes of Ag-Pd alloys. A decrease of the sintering temperatures and a considerable acceleration of the rate of densification can often be observed if a small amount of a liquid phase is present during the sintering process. In fact, it has been found that the sintering temperature of BaTiO$_3$ was lowered by small amounts of additives, such as lithium fluoride [92-93], borates [94] or copper oxide [95]. Therefore, additives in BaTiO$_3$ can not only modify the properties but also affect the sintering behavior.

For a number of years bismuth-containing compounds have been used with BaTiO$_3$ to reduce the sintering temperature, and Nb is known to reduce the Curie temperature. In this study, both Bi$_2$O$_3$ and Nb$_2$O$_5$ were mixed and sintered with BaTiO$_3$. Therefore, previous studies of Bi or Nb doped BaTiO$_3$ will be considered.

F. 1. Niobium-doped barium titanate

The dielectric properties of Nb-doped BaTiO$_3$ have been studied by several investigators. It was found that Nb greatly influenced the temperature dependence of the dielectric constant of BaTiO$_3$ [96-100]. With the addition of Ba$_{0.5}$NbO$_3$ from 0.02 to 0.08 mol%, Smolenski et al [98] found the permittivity maximum at the Curie point ($120^\circ$C) was retained but its magnitude was reduced. On
further increasing the amount of barium niobate (>1 mol%), the temperature-dielectric constant curve shows a lowered and broadened peak at lower temperatures, and the permittivity maximum at the temperature corresponding to the Curie point of pure BaTiO$_3$ disappeared.

The dielectric properties of solid solutions of BaTiO$_3$ containing niobium pentoxide (Nb$_2$O$_5$), metaniobate (Ba$_0.5$NbO$_3$) or pyroniobate (BaNbO$_{3.5}$) were studied by Subbarao and Shirane [99]. In their study the mixed material was sintered at temperatures between 1300 and 1450°C for 0.5 to 6 hrs. With the addition of Nb$_2$O$_5$, they found the Curie point of barium titanate was lowered proportional to the Nb$_2$O$_5$ content, and the temperature-dielectric constant curve showed a broadened peak, Fig. 10. Moreover, they found the tetragonal-orthorhombic transition was raised by about 17°C with the addition of 0.8% Nb$_2$O$_5$. The orthorhombic-rhombohedral transition was also found to shift upward by about 20°C with 0.04% Nb$_2$O$_5$. Furthermore, they observed that niobium oxide, metaniobate and pyroniobate had the same effect and they all formed solid solutions with BaTiO$_3$ and had a perovskite-type structure. The solubility limit of Nb was about 14 at%. With the addition of 3 to 4 mol% of NbO$_{2.5}$, the BaTiO$_3$ solid solution reverted to the cubic structure at room temperature and the lattice parameter of the cubic phase increased with the Nb content. While around 14 mol% Ba$_{0.5}$NbO$_3$ dissolved in BaTiO$_3$, the Curie temperature could be lowered to about
Fig. 10. Temperature dependence of dielectric constant of ceramic in the system (100-x) BaTiO$_3$+ x NbO$_2$.5 [99]
Using X-ray and neutron diffraction techniques the authors concluded that Nb substituted for Ti and created charge-compensating cation vacancies (Ba or Ti).

Kahn [100] studied the influence of grain growth on dielectric properties of Nb-doped BaTiO$_3$. He found that when substantial grain growth occurred in Nb-doped BaTiO$_3$, the dielectric constant curves showed single peaks and the Curie temperature shifted downward in proportion to Nb content. When only limited grain growth occurred, however, the dielectric constant vs temperature curves have two peaks. Due to the inhomogeneous distribution of Nb in samples with limited grain growth, he then attributed the peak at 122°C to residual Nb-free BaTiO$_3$ and the peak at low temperature to Nb-containing BaTiO$_3$. This observation confirmed the effect of Nb in modifying the intrinsic dielectric properties of BaTiO$_3$. According to his observation, the Curie temperature could be lowered to 45°C while the Nb concentration was about 5 at%. Another important observation in Kahn's study was that the distribution of Nb, which affected the dielectric property of BaTiO$_3$, was strongly controlled by grain growth.

The effect of grain growth on the distribution of Nb in BaTiO$_3$ was investigated by Buessem and Kahn [101]. By measuring Nb diffusion into large- and small-grained BaTiO$_3$, they concluded that Nb had a much higher grain boundary diffusivity than bulk diffusivity. Further they showed, using X-ray diffraction, that
homogeneous Nb-doped BaTiO$_3$ only existed when significant grain growth occurred. When grain growth was limited, both Nb-free and Nb-rich regions existed. Owing to the low bulk diffusivity of Nb, little Nb could penetrate into the original grain, and a Nb-containing solid solution formed only in the recrystallized regions. Buessem and Kahn then concluded that when grain growth was limited, a non-homogeneous system resulted; when appreciable grain growth occurred, an essentially uniform system was obtained.

Sintering temperature, sintering atmosphere and the concentration of Nb all affect the grain size in the final microstructure of sintered Nb-doped BaTiO$_3$ [102-105]. BaTiO$_3$ with Nb less than 0.35 at% grows into large grains when fired in air [104, 105]. When the Nb concentration exceeds 0.4 at%, niobium acts as a powerful grain growth inhibitor in air-fired BaTiO$_3$. It was also found that low partial pressure of oxygen favors grain growth. Furthermore, oxygen was released during sintering Nb-doped BaTiO$_3$ in vacuum and the amount of released oxygen was proportional to the Nb concentration [105]. When the Nb concentration was >0.4 at%, no oxygen was released during sintering in air.

Several other donors in BaTiO$_3$ such as Sc, Ta, La and Dy behave in a similar manner to Nb [106-110]. Above a certain dopant concentration, the microstructure remains fine grained. Even though the exact cause of grain growth inhibition in heavily donor-doped BaTiO$_3$ is still not very clear, it is generally agreed that the cation vacancies (possibly Ba vacancies) in BaTiO$_3$ lattice, which
compensate extra donor positive charges, play an important role [103, 105].

F. 2. Bismuth doped barium titanate

Bi$_2$O$_3$ is a widely used material in manufacturing BaTiO$_3$-based ceramic capacitors [111-112]. Since Bi$_2$O$_3$ has a low melting point (825°C), this material is commonly used to reduce the sintering temperature of BaTiO$_3$. Gawrychowska [113] studied the sintering of BaTiO$_3$-Bi$_2$O$_3$ powder mixtures and found sintering of this powder mixture started at 740°C, which corresponded to the melting point of a mixture with BaTiO$_3$/Bi$_2$O$_3$ ratio 2:3.

Swilman and Gadalla [114] and Baxter, et al. [115] also investigated the sintering behavior of Bi$_2$O$_3$-containing BaTiO$_3$. Swilman and Gadalla [114] found that at 1200°C the solubility of Bi$_2$O$_3$ in BaTiO$_3$ was only 0.23 mol%. BaTiO$_3$ sintered with 1 to 2 mol% (Bi$_2$O$_3$+1.5TiO$_2$) at 1400°C for 3 hrs., had a final relative density of only 85%.

Baxter, et al. [115] studied the sintering of BaTiO$_3$ with 5 mol% Bi$_2$O$_3$ and found after firing in the range of 1350 to 1420°C grain growth was limited (grain size=5um). The authors also found the sintered material remained tetragonal at room temperature, c/a=1.009 and c/a of BaTiO$_3$ is 1.010. In their study, they observed that the Curie temperature was raised by 9°C to 129°C, and the other
transitions were raised by 5°C.

$\text{Bi}_2\text{O}_3$ has also been used as a sintering aid to promote densification of strontium ferrite at lower firing temperatures [116]. Kolar and Drofenik [116] observed that the addition of $\text{Bi}_2\text{O}_3$ reduced the sintering temperature and increased the densification rate. However, when large amounts of $\text{Bi}_2\text{O}_3$ (5 to 10 mol%) were added, the density decreased at high temperatures (1000 to 1200°C) and also decreased with time at constant temperatures (1150 and 1200°C). In their study, weight loss was detected, and large pores were observed. The authors then attributed the density decrease in samples sintered at high temperatures or for longer times to the $\text{Bi}_2\text{O}_3$ volatization which formed large pores during sintering.
G. Temperature-Stable Dielectrics

There is an increasing need for temperature-stable dielectric materials to be used as ceramic multilayer capacitors. Unlike normal unmodified BaTiO₃, the high-permittivity materials needed for temperature-stable multilayer capacitors have to show abnormally flat dielectric constant-temperature curves so that the capacitance over the temperature range of use is stable. Practical temperature ranges of application have been specified from -55°C to 125°C. One type of temperature-stable dielectric, the X7R material, is specified by EIA (Electronic Industries Association) as having a dielectric constant that must not change by more than 15% from the 25°C reading over the temperature range -55 to 125°C.

High-quality temperature-stable dielectrics must have not only a small temperature dependence but also a high dielectric constant at room temperature. The temperature character of the permittivity is normally determined by the degree of chemical heterogeneity in these materials, whereas the value of the permittivity is affected by the grain size. Thus, in temperature-stable dielectrics, both the grain size and the distribution of the additives have to be controlled.

G. 1. Dielectric constant-temperature characteristics

BaTiO₃-based temperature-stable dielectrics have been previously studied [115, 117-119]. The dielectric constant-
temperature characteristic of several BaTiO$_3$-based X7R materials are given in Fig. 11. In BaTiO$_3$ containing 1 to 10 mol% NaNbO$_3$ and fired at 1420°C, flat dielectric constant curves result [115]. Baxter, et al. [115] observed that after sintering the average grain size was about 0.5 μm. The permittivity at room temperature was raised but it was decreased at the Curie temperature (120°C) resulting in a flat dielectric constant curve.

Burn [117] investigated the dielectric property of Nb$_2$O$_5$-doped BaTiO$_3$ and also studied the dielectric behavior of the Nb$_2$O$_5$-doped BaTiO$_3$ which was modified with small amounts of oxides of Co, Mg, Ni and Mn. All samples were sintered at 1400°C for 5 hrs. in air. When Nb$_2$O$_5$ was the only additive, the Curie temperature was decreased and a broadened permittivity peak was observed. A dense ceramic was obtained by adding 3.8 mol% NbO$_{2.5}$ but high porosity was observed with lower Nb$_2$O$_5$ content. With the addition of cobalt oxide the permittivity-temperature characteristic of Nb-doped BaTiO$_3$ was significantly changed. As the cobalt content increased, the presence of unreacted barium titanate became more evident, and a temperature-stable dielectric was achieved. On the other hand, as cobalt content was increased, the amount of porosity was increased. When similar amounts of TiO$_2$ and cobalt were added, densification was improved. Generally, magnesium oxide, nickel oxide and manganese oxide showed the same effect as cobalt oxide. They modified the niobium reaction with BaTiO$_3$ and resulted in a stable dielectric.
Fig. 11. Dielectric temperature characteristics of BaTiO$_3$-based X7R materials [119]. (I) BaTiO$_3$+0.03 mol $'_{3}$CdBi$_2$Nb$_2$O$_9$" sintered for 4 hrs. at 1130°C; (II) BaTiO$_3$+0.03 mol Bi$_4$Ti$_3$O$_{12}$ sintered for 4 hrs. at 1110°C; and (III) X7R-3000 sintered for 3 hrs. at 1300°C. (IV) Dielectric temperature characteristics of hot-pressed fine-grained BaTiO$_3$ (average grain size 0.52 μm) are shown for comparison.
Burn [117] found that, at least to about 5 mol% Nb, the distribution of niobium in the barium titanate grains could be regulated by small amounts (<1 mol%) of oxides of Co, Mg, Ni and Mn. These oxides appeared to form niobates that produced high permittivity solid solutions in the "skin" of barium titanate grains and produced dielectrics with permittivity $k' = 2000$, stable to within 10% over the temperature range -55 to 125°C. Moreover, the dielectric constant peaks in such modified Nb-doped BaTiO$_3$ were different from singly Nb-doped samples. With 3.8 mol% Nb dopant the peak maximum appeared at about 0°C. With increased cobalt content, a pure BaTiO$_3$ peak at 120°C was observed. In addition two extra peaks at 30 and -55°C were seen in the temperature-stable dielectric curves, Fig. 12.

Rawal, et al. studied the donor-doped barium-bismuth titanate system [118] and observed a stable dielectric curve. In their study the ceramics contained BaTiO$_3$ with 10 wt% Bi$_4$Ti$_3$O$_{12}$ and 3 wt% of a donor dopant. From the dielectric constant-temperature curve, they concluded there were two main peaks one at 110°C and the second one at room temperature.

BaTiO$_3$ sintered with 0.03 mol of the pseudophase "CdBi$_2$Nb$_2$O$_9"$ was investigated by Hennings and Rosentein [119]. A similar flat dielectric constant curve was observed except the relative dielectric constant at room temperature was different (see Fig. 11).
Fig. 12. Influence of cobalt oxide on the distribution of Nb (3.8 m/o) in barium titanate sintered at 1400°C 5 hr.
Rawal, et al. [118] and Hennings [119] interpreted the dielectric properties of these temperature-stable dielectrics as a combination of pure, fine-grained BaTiO₃ and a second dielectric material showing a dielectric Curie maximum at a lower temperature. In addition they characterized the dielectric behavior by using the 'Lichtenecker formula':

\[ \log k' = V_1 \log k'_1 + V_2 \log k'_2 \]  \hspace{1cm} (3)

where \( k' \) is the dielectric constant of the two phase mixture, \( k'_1 \) and \( k'_2 \) are the dielectric constants of the two phases and \( V_1, V_2 \) are the volume fractions.

The proposal that the temperature-stable dielectric behavior results of a two phase structure, consisting of relative pure barium titanate and an additive-containing phase with a lower Curie point, has been generally accepted by previous investigators [117-119]. This proposal originated from the dielectric behavior of the temperature-stable dielectrics, which showed two or three permittivity peaks at the temperature ranges of 120-140°C, 0-25°C and -60°C.

G. 2. Microstructural investigations

In a number of temperature-stable dielectric materials so-called "grain core-grain shell" structures have been found [118-122], as shown in Fig. 13. These materials exhibit chemically
Fig. 13. Transmission electron micrograph of BaTiO$_3$+0.03 mol "CdBi$_2$Nb$_2$O$_9$" sintered for 3 hrs. at 1200°C, showing the core-shell structure [119].
heterogeneous grains consisting of two phases at room temperature. The grain core consists of relatively pure BaTiO$_3$ showing typical ferroelectric domain patterns. The grain shell, on the other hand, was non-ferroelectric at room temperature containing most of the dopants.

Rawal, et al. [118, 120] investigated the donor-doped barium-bismuth titanate. They used Energy Dispersive Spectroscopy (EDS) to show that after firing at $1100^\circ$C the Bi concentration rapidly increased toward the grain boundary, and bismuth could diffuse into the grain cores at higher temperatures. The samples studied contained 10 wt% (about 2.2 mol%) Bi$_4$Ti$_3$O$_{12}$ and 3 wt% donor (Nb, La). Analytical Electron Microscopy (AEM) analysis showed no second phase on the grain boundaries and grain corners. In addition, electron diffraction of the grain cores and grain shells did not reveal measurable differences in the lattice dimensions between these two regions. Furthermore, by using X-ray diffraction analysis, they concluded that the impurity-containing shell was cubic at room temperature.

Mecartney, et al. [121] studied three types of X7R capacitors, with Bi or Zr as the major additives, and found an increased impurity content near the grain boundary. However, no distinct second phase was observed on the grain boundary or in the nonferroelectric regions. In addition, high resolution lattice imaging was performed at the grain boundaries and confirmed that no second phase existed down to a width of 1-2 nm. Using EDS analysis
inside the grain with a ferroelectric core they found an additive gradient in the non-ferroelectric regions, slightly increasing toward the grain boundaries.

Dopant enrichment at grain boundaries was observed by Hennings and Rosenstein [119] in samples sintered with 0.03 mol \(\text{CdBi}_2\text{Nb}_2\text{O}_9\) at 1130°C. A remarkable increase of homogeneity was observed when the sintering temperature was increased to 1320°C. They also found that evaporation of \(\text{Bi}_2\text{O}_3\) and \(\text{CdO}\) made the average concentration of Bi and Cd in the grains decrease monotonically with increasing temperature, whereas the concentration of Nb was unchanged.

The structure of the barium titanate ferroelectric-paraelectric transformation interface at the transition temperature \((T_c)\) was studied using TEM by Mallis and Gleiter [63, 64]. In their work, in situ heating tests were conducted on single-crystal and polycrystalline \(\text{BaTiO}_3\). The structure of the paraelectric region, ferroelectric domain regions and the interface between them were studied in detail.

It was found by Malis and Gleiter [63] that the ferroelectric domains were normally stable with increasing temperature until \(T_c\) was reached. At \(T_c\), the transformation of \(\text{BaTiO}_3\) from the ferroelectric tetragonal phase to the paraelectric cubic phase took place, and the transformation was indicated in TEM by the disappearance of the domain walls. The transformation process was
reversible and a decrease of the temperature resulted in domain growth. In addition, they found that transformation occurred only at $T_c$. Small temperature increases of the order of a degree or less above $T_c$ would move the transformation interface progressively until no trace of the domains remained.

In polycrystalline samples, the transformation interface migration could be halted for several hours of observation at any point by stabilizing the temperature. In contrast, the mobility of the interface in the single-crystal specimen was much greater and the interface would not remain stable more than a few minutes when the temperature was held constant.

Malis and Gleiter [63] found that under no diffraction conditions was there any fringe contrast between the region of the domains and that where domains had disappeared, in either single-crystal or polycrystalline specimens. In addition by monitoring the split of Kikuchi lines (arising from splitting of the diffraction spots), they found that Kikuchi line splitting decreased with the distance from the transformation interface and no splitting was observed in the paraelectric region about 1 um away from the interface. Therefore, a broad diffuse-interface model was proposed by the authors [63]. In that model, they proposed the lattice cells underwent a continuous tetragonal-cubic transition across the transformation interface, as schematically illustrated in Fig. 14, and the effective width of the transformation interface was of the order of microns. This interface, therefore, might be described as
Fig. 14. Schematic diagram of the unit cell transformation across the ferroelectric-paraelectric interface in BaTiO$_3$. Note the tetragonality is exaggerated by a factor of more than 400 for illustrative purpose [63].
an elastically forced coherent interface. The absence of interphase boundary fringes or dislocations was thus explained by the small misfit between the cubic and tetragonal phase (c/a* = 1.005 at Tc [63]) and the broad interface regions.

The work done by Malis and Gleiter [63] illustrated the complete coherence between the ferroelectric and paraelectric phase, and the model they proposed clearly explained the observed TEM results. The same broad diffuse interface model may also be applied to explain the observed core-shell interface. In previous studies, complete coherence between the grain core and grain shell had been observed. Similarly, no boundary fringes or dislocations were observed on the core-shell interface. In their study, pure BaTiO₃ was used, and their results showed that the transformation of the ferroelectric domains was independent of time and was dependent on the temperature over a range of a few degrees. Even though they did not consider compositional effects on the ferroelectric to nonferroelectric transformation their interface structure model may still apply.

G. 3. The formation mechanism of core-shell structure

The crucial problem in the preparation of X7R materials is the formation of chemically inhomogeneous perovskite. In general, additives and dopants soluble in the perovskite are incorporated during grain growth and densification. A model of the core-shell
structure formation mechanism was proposed by Hennings, et al. [119].

Hennings, et al. [119] proposed that in BaTiO$_3$ containing "CdBi$_2$Nb$_2$O$_9" additives, densification and grain growth are largely determined by liquid-phase sintering. Owing to the observation of a large number of endothermic and exothermic peaks in Differential Thermal Analysis (DTA), they supposed that the liquid phase formed during sintering. Since the shapes and the number of the DTA peaks could not be attributed to any known phase diagram and the peaks changed from one cycle to the next, they claimed a reactive sintering process, which is not thermodynamically stable, occurred during sintering.

Following these DTA observations they then assumed that the core-shell structure was formed through a solution-precipitation process. At the beginning of the sintering, due to the small amount of additives, large BaTiO$_3$ grains remain or are partially dissolved. During the solution-precipitation process the smaller BaTiO$_3$ particles are completely dissolved. The larger particles, on the other hand, grow by precipitation of perovskite from the melt. When perovskite precipitates from the melt it contains Cd, Bi and Nb, and the larger particles of pure BaTiO$_3$ become the cores which are embedded in the perovskite shell containing the dopants. During precipitation of perovskite, more and more of the additives pass
from the liquid phase into the solid material of the shell, which leads to an increase of the melting temperature and, finally, to freezing of the liquid phase. The coherence of the lattice of core and shell was confirmed by electron diffraction in the TEM.

Rawal, et al. [120] considered the formation of the core-shell structure in donor-doped bismuth-barium titanate. They proposed that the relatively pure barium titanate grain cores came from the original powder and served as nucleation centers during sintering. The impurity-containing grain shell, where the BaTiO$_3$ reacts with the soluble additives, formed during grain growth. In addition, the fast rate of dopant grain boundary diffusion was responsible for the homogenization of the impurity-containing shell during sintering. No suggestion of liquid formation was invoked by Rawal, et al. to explain the core-shell structure.

Even though the formation mechanism of the core-shell structure has been discussed by previous investigators no conclusive results have been presented and the actual formation mechanism is still not clear.
CHAPTER III
EXPERIMENTAL PROCEDURES

A. Powder Processing

Ticon HPB BaTiO$_3$ powders, supplied by TAM Ceramics, Inc., Niagara Falls, N Y, were used throughout this study. TAM Ceramics prepares the HPB powder using a chemical precipitation technique. The X-ray diffraction pattern (XRD) of the starting BaTiO$_3$ powder is given in Fig. 15 for 2$\theta$=20-50°. This diffraction pattern can be indexed as tetragonal BaTiO$_3$, belonging to the space group P4/mm (JCPDS card # 5-0626). Fig. 16 is a bright-field TEM image of agglomerated BaTiO$_3$ powder; the particle size (measured by the Zeiss "Videoplan" particle analysis system) ranged from 0.1 to 1 um with an average value of 0.35um. The BaTiO$_3$ powder exhibited a rounded morphology and domain fringes were observed in some particles.

High purity (99.999%) Bi$_2$O$_3$ and Nb$_2$O$_5$ powders were purchased from Johnson Mathey Chemicals Ltd., Hertfordshire SG8 5HE, England. Nb$_2$O$_5$ powders were also agglomerated and the size of these agglomerates were about 1.5-3 um with each individual particle 0.4 um, as shown in the secondary electron SEM image of Fig. 17. Bi$_2$O$_3$ powders were well separated and had an average diameter of 1 um (Fig. 18). The XRD patterns of the initial Nb$_2$O$_5$ and Bi$_2$O$_3$ powders
Fig. 15. XRD of initial BaTiO₃ powder.
Fig. 16. TEM images of BaTiO$_3$ powder.
Fig. 17. Secondary electron SEM image of Nb$_2$O$_5$ powder.

Fig. 18. Secondary electron SEM image of Bi$_2$O$_3$ powder.
are shown in Fig. 19 and 20; both of them had a monoclinic crystal structure (space group A2/a and P2₁/c respectively). The JCPDS cards used to index Nb₂O₅ and Bi₂O₃ were 16-53 and 27-53.

The procedures and powder compositions employed during processing are shown in Fig. 21. Different amounts of the dopants, Bi₂O₃ and/or Nb₂O₅, were wet mixed with pure BaTiO₃ powder. The wet mixing step was accomplished by placing approximately 75 grams of powder mixture in a 500 ml polyethylene container with isopropyl alcohol and aluminum cylinders as mixing media. After 15 hours mixing, the slurry was dried in a convection oven at 90°C for 10 hours. The mixed raw material was then ground into powder in a mortar and pressed into pellets by using a hydraulic press at a pressure of 15,000 psi (10.34 MPa). The pressed pellets were 0.55 inch (13.4 mm) in diameter and approximately 0.2 inch (5.1 mm) thick.

To facilitate microstructural investigation, samples containing large BaTiO₃ particles (3-10 μm) were prepared using similar procedures to those described above. However, 5 wt% of large diameter BaTiO₃ particles (3 to 10 μm) were additionally mixed with the original powders, while maintaining the total composition of the powder mixture. These large BaTiO₃ particles were obtained from sintered pure BaTiO₃ pellets. Pure BaTiO₃ pellets were sintered at 1400°C for 2 hrs. and then crushed and milled in a mortar. The particles were dispersed in distilled water and then classified into
Fig. 19. XRD pattern of Nb$_2$O$_5$ powder.
Fig. 20. XRD pattern of Bi$_2$O$_3$ powder.
BaTiO$_3$ + $X$ mol Bi$_2$O$_3$ + $Y$ mol Nb$_2$O$_5$

$X$=0.05, $Y$=0.05  
$X$=0.03, $Y$=0.03  
$X$=0.00, $Y$=0.00  
$X$=0.10, $Y$=0.00  
$X$=0.00, $Y$=0.10

↓

wet mixed in isopropyl alcohol 15 hrs.

↓

dried at 90°C 10 hrs.

↓

Pressed into pellets (15,000 psi)

Fig. 21. Processing Procedures.
four fractions of different sizes by a sedimentation technique. The fraction with particle size ranging from 3 to 10 µm, as shown in Fig. 22, was collected and used.

B. Sintering

A Lindberg tube furnace was used for heat treatment, and the pressed pellets were placed on a platinum foil during sintering to avoid reactions between the samples and the tube or the refractory. Samples were sintered at temperatures between 1100 and 1300°C for 0.5 to 100 hrs. The heating and cooling rates were set at 10°C/min, and the atmosphere was air.

To determine the composition of sublimed solid during sintering, five BaTiO₃ pellets with 0.05 mol Bi and Nb dopants were placed on a platinum foil and inserted into a quartz tube. The whole assembly was then put in the tube furnace and fired at 1150°C for 40 hrs. During this treatment the sublimed material reacted with the quartz and formed a white reaction layer on the inner surface. EDS chemical analysis was performed to investigate the composition of this reacted surface layer.

Reaction between pure BaTiO₃ pellets with Bi₂O₃ and Nb₂O₅ was also studied. Pressed BaTiO₃, embedded in the powder mixture of Bi₂O₃ and Nb₂O₅ with equal mole percentage, was fired at 1150°C for 1 hr. After firing the surrounding powder was examined by XRD.
Fig. 22. Secondary electron SEM images of large BaTiO$_3$ particles.
C. Density Determination

The densities of the sintered and slowly cooled (10°C/min) samples were determined by an immersion technique and were calculated using the Archimedes principle. A dry sample was first weighed and then submerged in distilled water for 15 minutes. The saturated weight of the sample after submerging in the water was measured. After that, the sample, which was suspended in a wire basket, was then weighed in distilled water.

Density calculation followed the formula given below:

$$\text{density} = \frac{\text{Wt.(dry)} \times \text{D(liq)}}{\text{Wt.(saturated)} - \text{Wt.(suspended)}}$$

(4)

where Wt.(dry) was the weight of a dry sample, Wt.(saturated) was the weight of a sample after submerging in distilled water, Wt.(suspended) was the sample's weight in distilled water and the density of distilled water, D(liq), is 1.

D. X-ray Diffraction Analysis

X-ray diffraction (XRD) analysis was performed on powders using a "Sintag Pad-5" diffractometer or a Philips 3100 X-ray diffractometer, Eindhoven, The Netherlands. For both of the diffractometers, Cu Kα radiation was used. The Philips diffractometer was operated at 40 kV and 30 mA and the scanning rate
was 2° two theta per minute. With the "Sintag Pad-5" diffractometer, 30 kV and 30mA were used and the scanning rate was 1° per minute in low angle regions (20-80°) and 0.2° per minute in high angle regions (98-120°). JCPDS card number 16-486 was used to index BiNbO₄.

The lattice parameter determination was performed using the "Sintag Pad-5" diffractometer" with a scanning rate 0.2° per minute in high angle region (98-120°). According to JCPDS card # 5-0626, the unit cell dimensions of a tetragonal BaTiO₃ at 26°C are 3.994 Å along a axis and 4.038 Å along c axis. The wavelengths of Cu Ka₁ and Cu Kα₂ were calibrated using the (400), (114) and (204) peaks of 1200°C 2 hrs sintered pure BaTiO₃. Since the interplanar spacings of pure BaTiO₃ could be calculated using a=3.994 and c=4.038 and the angle of each peak could be determined from the XRD, the wavelengths of Kα₁ and Kα₂ could then be calculated by Bragg’s law, \( \lambda = 2d \sin \theta \). The calculated wavelengths of Cu Ka₁ and Cu Kα₂ were 1.54056±0.0078% and 1.54439±0.025%. The average wavelengths of Kα₁ and Kα₂, 1.54056 and 1.54439, were used to determine the lattice parameters of the 0.03 and 0.05 mol (Bi₂O₃+Nb₂O₅) doped and 1150°C 100 hrs. sintered BaTiO₃. Since the X-ray acquisition increment was 0.03°, the scattering of X-ray peak in high angle region (98-120°) should be less than 0.02%. The lattice parameters of 0.03 and 0.05 mol doped samples were calculated from the (400), (410), (411), (313) and (204) peaks. The averaged value from those peaks was taken as the lattice parameter of each sample and the deviation of it was less than 0.1%.
E. Thermal Analysis

Differential thermal analysis (DTA) was conducted on a Perkin-Elmer DTA 1700 Differential Thermal Analyzer, Norwalk, CT. which was connected to System 7/4 Thermal Analysis Controller and a Perkin-Elmer graphic plotter. In the DTA experiments, powder (pure BaTiO₃ powder or dopant-containing and mixed powder) was used and coarse Al₂O₃ was used as the reference. The heating rate was controlled at 5°C/min and the atmosphere was air.

Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA 7 Thermogravimetric Analyzer controlled by a PE 7500 Professional Computer. Weight loss was recorded as a function of temperature or time for a linearly controlled heating rate of 10°C/min in air. Shrinkage of pressed pellets during heating was measured with an Orton Automatic Recording Dilatometer. The linear dimensional change as a function of temperature was measured on samples heated in air at a rate 10°C/min.

F. Dielectric Measurements

The dielectric constant (k') of samples with different composition and heat treatment was measured at TAM Ceramics Inc., Niagara Falls, New York. Before the measurements were made, sintered disk samples were polished to 600 mesh SiC grit on both surfaces. During polishing, a South Bay Technology (Temple City, California)
Lapping Fixture was used to keep the surfaces flat and parallel to each other. After polishing, silver electrodes were hand painted on both surfaces and heated at 150°C overnight to enhance the adherence.

All samples were mounted in a Saunders and Associates, Inc., Scottsdale, Arizona, test wheel and placed in a Saunders 4200 A Test Chamber. Through a Saunders 2211 A Process Controller, capacitance of each sample was measured by an Electron Scientific Industries, Inc.'s Video Bridge. The capacitance of each sample was measured at a fixed frequency 1 KHz at temperatures from -55°C to 125°C. The relative dielectric constant, $k'$, was then calculated by the equation

$$k' = \frac{C \times t}{A \times \varepsilon_0}$$

(5)

where $A$ was the area of the electrode, $\varepsilon_0$ the permittivity of vacuum, 8.854x10^{-12} F/m, and $t$ the thickness of the sample tested.

G. Microstructural Examination

The microstructure of sintered samples was examined with an ISI-SX 40 Scanning Electron Microscope (SEM), Milpitas, California, and a JEOL 200-CX Transmission Electron Microscope (TEM), Peabody, Massachusetts, with a Tracor-Northern TN 2000 EDS system, Middletown, Wisconsin.
For SEM analysis, sintered samples were cut into halves, ground using SiC grit of 320, 400 and 600 mesh and polished with 6μm, 3μm, 1μm and 1/4μm diamond pastes. After polishing, the sample surface was cleaned with acetone in an ultrasonic bath. Polished surfaces were then etched for two minutes using 5 vol.% HCl in H₂O with several drops of 48% HF. The etched sample surface was then sputter-coated with gold to avoid charging. Secondary electron imaging was used to reveal contrast due to surface topography.

To prepare thin film specimens for TEM examination, the sintered samples were first cut into thin slices, about 1mm thick, using a Buehler Ltd., Lake Bluff, Illinois, diamond-impregnated saw and then cut into 3mm diameter disks with a Gatan Model 601 Ultrasonic Disc Cutter, Gatan Inc., Warrendale, PA. These 3mm disks were mechanically polished down to about 100μm thick and the central part of the polished disks was further thinned by dimpling on a stainless steel ball. During dimpling, 6μm, 3μm, 1μm and 1/4μm diamond paste acted as the abrasive and the disk center was kept about 30μm thick.

Dimpled 3mm discs were then ion milled using a Gatan Model 600 Duo Mill by bombarding both surfaces with Ar⁺ ions at an angle 10-15°, a voltage of 5.5 kV and a current of 1 mA until a hole formed. The regions near the hole edge were then electron transparent.
For TEM investigation, specimens were placed either in a double-tilt holder or a temperature-controlling holder. The double-tilt holder facilitated specimen tilting about orthogonal axes so that the investigated area could be examined in various orientations. In comparing the crystal structures of grain core and grain shell or identifying the planar defects in the grain shell, the double-tilt holder was used.

To investigate the existence of domains in the ferroelectric grain core and comparing the crystal structures of the core and shell, the electron diffraction patterns of the core and shell were recorded with a well defocused C2 lens. To examine the planar defects in the grain shell, TEM bright-field (BF) and dark-field (DF) images at different reciprocal lattice vectors, g vectors, were recorded and compared. The fringes in the BF and DF images were then used to characterize the planar defects in the grain shell.

The temperature-controlling holder enabled the specimen to be set at a specific temperature. In this study the temperature range was from -174 to 140°C. The specimen was placed in a specimen retainer in this holder and a Cu-constantan thermocouple was used to measure the temperature. An electric resistance heater and liquid nitrogen refrigerant were used to control the specimen's temperature. Usually, the specimen was held at a specific temperature for at least 30 minutes before microstructural examination or chemical analysis; thus thermal equilibrium could be reached and image shifting could be avoid.
The Zeiss "Videoplan" particle analysis system was used to measure the grain size and the core size. High magnification TEM BF images were used for this measurement, so that the grain boundaries and the grain cores were clearly illustrated. The number of grains counted in each sample ranged from 30 to 150. The count, standard deviation and mean of each sample's grain and core sizes are listed in Appendices VII and VIII. The mean is taken as the average value. The deviation of the average value is the square root of 1/count. In these measurements, the deviations of the average core and grain sizes are in the range of 8 to 18%.

H. Chemical Analysis

Energy dispersive spectroscopy (EDS) was performed for qualitative and semi-quantitative chemical analysis using a Tracor-Northern TN 2000 EDS system attached to the JEOL 200-CX STEM and a probe diameter about 2 nm. For qualitative analysis, the elements present were identified by their characteristic X-ray spectrum. However, in Bi and Nb doped BaTiO₃, extensive peak overlap occurs between Ba La lines and Ti Ka lines. Semi-quantitative chemical analysis was possible by measuring the counts in Bi(Lα) peak (10.48-11.08 keV), Nb(Kα) peak (16.28-16.80 keV) and the overlapped Ba(Lα) +Ti(Kα) peak (4.20-4.68 keV). The count ratios of Bi(Lα) to Ba(Lα) +Ti(Kα) and Nb (Kα) to Ba(Lα)+Ti(Kα) were then calculated and plotted to show the relative concentrations of Nb and Bi and their
In evaluating the count ratios, that is, the ratios of the X-ray counts, we encounter a source of statistical error. This statistical deviation arises from the statistically independent emission and the subsequent detection of a characteristic X-ray, which has a fixed probability of occurring within each counting time interval. This relative standard deviation is inversely proportional to the square root of the average counts. In this work, the counts in Bi(\(\text{L}_{\alpha}\)) and Nb(\(\text{K}_{\alpha}\)) peaks were about 500 to 1000, and the count in Ba(\(\text{L}_{\alpha}\))+Ti(\(\text{K}_{\alpha}\)) peak was about 20,000. Therefore, the standard deviation of the count ratios in this work should be less than 5%. In fact, the measured deviations of the Bi(\(\text{L}_{\alpha}\))/Ba(\(\text{L}_{\alpha}\)+Ti(\(\text{K}_{\alpha}\)) and Nb(\(\text{K}_{\alpha}\))/Ba(\(\text{L}_{\alpha}\)+Ti(\(\text{K}_{\alpha}\)) count ratios at the core-shell boundaries were about 5% and 10% respectively.

In an attempt to quantify the mole percentage of Ba, Ti Bi and Nb in the grain shells and the grain cores, the EDS spectra obtained from those areas were compared to the spectra from pure Ba\(\text{TiO}_3\), Ba\(\text{CO}_3\), Ti\(\text{O}_2\), Bi\(\text{O}_3\) and Nb\(\text{O}_5\). However, no successful results were obtained due to: the instrument's temperature sensitivity; calibration deviation and spectra misfitting. The major problem in this approach is fitting the Ba+Ti peak of Ba\(\text{TiO}_3\) by the Ba peak of Ba\(\text{CO}_3\) and the Ti peak of Ti\(\text{O}_2\). After spectrum fitting and subtraction, the residual counts in the main peak, Ba(\(\text{L}_{\alpha}\))+Ti(\(\text{K}_{\alpha}\)),
were more than 1/3 of the original counts. Consequently, the results obtained by this approach were questionable, and accurate quantification of Bi and Nb was unsuccessful.
In this chapter results concerning sintering, dielectric properties and microstructural characterization are presented. Most of the results were obtained from the samples doped with Bi$_2$O$_3$ and Nb$_2$O$_5$, but pure BaTiO$_3$ or BaTiO$_3$ only doped with Bi$_2$O$_3$ were also studied for comparison. Analytical electron microscopy was used for microstructural analysis. Microstructural evolution, structural characteristics and dopant distributions were studied extensively and will be presented in this chapter.

A. Sintering

BaTiO$_3$ sintered with various combinations of Bi$_2$O$_3$ and Nb$_2$O$_5$ has been extensively studied. With 0.05 mol. Bi$_2$O$_3$ + 0.05 mol Nb$_2$O$_5$ BaTiO$_3$ could be sintered at a low temperature, 1100°C. However, the density progressively decreased as sintering time or temperature increased. Associated with such a density decrease was a weight loss and Bi was detected in the evaporated species. In addition, large pores formed in samples sintered at higher temperatures and for longer times. In this section, the results of binary-doped BaTiO$_3$ will be presented and compared to data of pure BaTiO$_3$, and BaTiO$_3$
with only one dopant added.

A. 1. Shrinkage

The shrinkage of BaTiO$_3$ sintered with Bi$_2$O$_3$ and/or Nb$_2$O$_5$ was studied with a dilatometer at a heating rate 10°C/min. As shown in Fig. 23(a), with 0.05 mol. of both dopants, BaTiO$_3$ sintered to high density at a low temperature (1100-1150°C) with about 15% linear shrinkage. With 0.03 mol of both dopants, high density was also achieved at low temperature (1200°C), Fig. 23(b). However, pure BaTiO$_3$ could only be sintered to high density above 1300°C, Fig. 24(a).

The addition of 0.1 mol. Nb$_2$O$_5$ did not change the shrinkage behavior of BaTiO$_3$, Fig. 24(b), but addition of 0.1 mol Bi$_2$O$_3$ did (Fig. 25). With 0.1 mol. Bi$_2$O$_3$ in BaTiO$_3$, densification started at about 720°C. After 5% linear shrinkage, densification became very slow and only 10% shrinkage was observed after heating to 1350°C.

In contrast to pure BaTiO$_3$ and BaTiO$_3$ with 0.1 mol. Bi$_2$O$_3$, as illustrated in Fig. 26, the 0.05 mol. binary doped samples rapidly densified at 1100°C and no shrinkage was detected in the 700 to 800°C range. Therefore, densification of the binary-doped system cannot be attributed simply to the melting of Bi$_2$O$_3$ and its shrinkage behavior but is a synergistic effect of both Bi$_2$O$_3$ and Nb$_2$O$_5$ additions.
Fig. 23. Shrinkage behavior of BaTiO₃ with (a) 0.05 and (b) 0.03 mol (Bi₂O₃+Nb₂O₅).
Fig. 24. Shrinkage behavior of (a) BaTiO₃ and (b) BaTiO₃+0.1 mol Nb₂O₅.
Fig. 25. Shrinkage of BaTiO$_3$ with 0.1 mol Bi$_2$O$_3$. 
Fig. 26. Comparison of the shrinkage behavior of BaTiO$_3$ with or without dopants.
A. 2. Density

Densities of $\text{Bi}_2\text{O}_3$ and $\text{Nb}_2\text{O}_5$-doped and slowly-cooled samples were calculated using the Archimedes principle, and the results are listed in appendices I-III. The highest density ($5.74 \text{ g/cm}^3$) was observed for the 0.05 mol. doped $\text{BaTiO}_3$ at 1150°C after no hold at the sintering temperature (0 hr.), as shown in Fig. 27. Longer sintering times led to decreased density, and the density of a sample sintered for 40 hrs. at 1150°C was only 4.755 g/cm$^3$. Samples with 0.03 mol dopants showed the same trend at this sintering temperature, although they showed less of a density decrease and always had higher density.

In contrast, $\text{BaTiO}_3$ with 0.01 mol dopant additions showed quite different behavior (Fig. 27). At 1150°C the density steadily increased with sintering time from its very low starting value ($4.15 \text{ g/cm}^3$). Even after 40 hrs. the density was still low, 5.32 g/cm$^3$.

For samples of the same composition, sintering temperature also affected the final density. With 0.05 mol dopants, the samples fired at 1100°C always had higher density than those fired at 1150°C (Fig. 28). Although longer sintering time always resulted in lower density, a lower sintering temperature gave a smaller density decrease as sintering time increased.

In Fig. 29 densities of samples sintered for one hour at different temperatures are compared. For the 0.05 mol. doped samples, the highest density was obtained at a sintering temperature of 1100°C ($5.78 \text{ g/cm}^3$). Higher sintering temperatures
Fig. 27. Effect of composition and sintering time on density. The heating and cooling rates were 10°C/min.
Fig. 28. Effect of sintering temperature and time on density.

Fig. 29. Effect of composition and sintering temperature on density for samples all fired 1 hr.
dramatically decreased the final density, and density of the sample sintered at 1250°C was only 4.95 g/cm³. For the 0.03 mol. doped samples, however, the effect of temperature was not so drastic. Densities did not change much after the sintering temperature reached 1150°C.

Sintering time, temperature and the dopant content all affected the final density of sintered samples. From the results presented above, it can be clearly seen that, with 0.03 or 0.05 mol. dopants, longer sintering times and higher sintering temperatures result in lower density. In addition, lower density was observed in samples doped with 0.05 mol. (Bi₂O₃ + Nb₂O₅) above 1150°C (see Fig. 29). The density of the 0.1 mol Bi₂O₃-doped sintered sample was also low. After 40 hrs. sintering at 1150°C, the measured density was 5.224 g/cm³.

A. 3. Pore formation and swelling

The microstructures of samples with 0.05 mol dopants were examined in an SEM to determine the reason for the density variation with sintering time and temperature. Fig. 30 and 31 clearly showed that after sintering at 1150°C for 1 hr. small pores (3-10 μm) were homogeneously distributed within the sample, but larger pores (30-400 μm) were observed after sintering for 40 hrs. Similarly, large pores also formed in the sample fired at high temperature, 1250°C, as shown in Fig. 32. The formation of these large pores in the
sample upon sintering at higher temperature or longer time, resulted in the density decrease.

In the 0.1 mol Bi$_2$O$_3$-doped and 1150°C 40 hrs sintered sample, some large pores were also observed, as shown in Fig. 33. The size of the pores in this Bi$_2$O$_3$-doped sample was in the range of 30-100 μm. For samples sintered at 1150°C for 40 hrs, the pore size of the 0.1 mol Bi$_2$O$_3$-doped sample is smaller than that of the 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$)-doped sample (see Fig. 30, 31, 33). However, compared to the pore size of 0.05 mol binary doped and 1150°C 1 hr. sintered sample (3-10 μm), the pore size of 0.1 mol Bi$_2$O$_3$ doped sample is still large (see Fig. 30, 31 33).

Fig. 30 and 33 show that most of the pores appeared in the interior of the sintered ceramics, but less or no pores existed close to the sample edges. This phenomena occurred in all the samples, and most of the pores were round-shaped closed pores.

As well as density decrease and pore formation, the Bi and Nb doped samples swelled up during sintering (see Appendix I and II). For example, the diameter of the 1150°C sintered and 0.05 mol binary doped sample increased from 11.850 mm of the 0.5 hr. sintered sample to 12.470 mm of the 100 hrs. sintered sample. In general, during sintering of the binary doped samples, the dimensional expansion was associated with the density decrease. Higher sintering temperatures and longer sintering times resulted in more swelling and lower density.
Fig. 30. Secondary electron SEM images (near surface) of 0.05 mol doped samples sintered at 1150°C for (a) 1 and (b) 40 hrs.
Fig. 31. Secondary electron SEM images (interior) of 0.05 mol doped samples sintered at 1150°C for (a) 1 hr. and (b) 40 hrs.
Fig. 32. Secondary electron SEM images of 0.05 mol doped sample sintered for 1 hr. at 1250°C.
Fig. 33. Secondary electron SEM images of 0.1 mol Bi$_2$O$_3$ doped BaTiO$_3$ sintered at 1150°C for 40 hrs.
A. 4. Weight loss

TGA confirmed that Bi$_2$O$_3$ was a volatile compound. After heating to 1400°C at a rate of 10°C/min, more than 70% of the initial Bi$_2$O$_3$ powder evaporated (Fig. 34a). At 1150°C, the weight loss of pure Bi$_2$O$_3$ was also considerable (about 2.5%), Fig. 34b. In contrast to Bi$_2$O$_3$, BaTiO$_3$ and Nb$_2$O$_5$ were far more stable. After heating to 1400°C little weight change was detected in BaTiO$_3$ or the mixture of BaTiO$_3$ and 0.1 mol. Nb$_2$O$_5$ to 1400 °C, as shown in Fig. 35.

Significant weight loss was observed for BaTiO$_3$ containing Bi$_2$O$_3$, Fig. 36. After heating to 1150°C 1.35% loss was detected, and more than 16% of the initial weight was lost at 1400°C. Moreover, the wt% loss (16.3%) during heating to 1400°C was close to the wt% of Bi$_2$O$_3$ in the initial powder mixture (16.65%).

For the powder mixture of BaTiO$_3$ with 0.05 mol (Bi$_2$O$_3$ + Nb$_2$O$_5$), a small weight loss was detected during heating, as shown in Fig. 37. At 1150°C about 0.6 wt% was lost and 4.7 wt% was lost at 1400°C. Since the wt% of Bi$_2$O$_3$ in this powder mixture was 8.365, it appears that not all of the Bi$_2$O$_3$ was lost or evaporated at 1400°C. Furthermore, when the powder mixture of BaTiO$_3$ with 0.05 mol. dopants was held at 1150°C, considerable weight loss was also observed with time, Fig. 38. Longer heating time caused more weight loss, and around 4.6 wt% was lost after heating for 10hrs.
Fig. 34. TGA of Bi$_2$O$_3$ from (a) 100 to 1400°C and (b) 200 to 1150°C.
Fig. 35. TGA of (a) BaTiO$_3$ and (b) BaTiO$_3$+0.1 mol Nb$_2$O$_5$. 
Fig. 36. TGA of BaTiO$_3$+0.1 mol Bi$_2$O$_3$ from (a) 200 to 1150°C and (b) 100 to 1400°C.
Fig. 37. TGA of BaTiO\textsubscript{3} with 0.05 mol (Bi\textsubscript{2}O\textsubscript{3}+Nb\textsubscript{2}O\textsubscript{5}) from (a) 200 to 1150°C and (b) 100 to 1400°C.
Fig. 38. TGA of BaTiO$_3$ with 0.05 mol dopants heated at 1150°C for 10 hrs.
From the TGA results shown above, it is confirmed that Bi$_2$O$_3$ is a volatile compound, and significant weight loss occurred in Bi$_2$O$_3$-containing powder mixtures. In addition, weight loss was increased by higher heating temperature or longer heating time.

To investigate the nature of the weight lost, EDS chemical analysis was conducted. Since the evaporated species reacted with the quartz tube, EDS analysis was performed on the ground powder of the reacted layer. As shown in Fig. 39, Bi was detected and no Nb, Ba or Ti was observed. The detected Cu was from Cu specimen grid; Si was from quartz and Y was also possibly from the quartz tube.

A. 5. Reactions

The occurrence of reactions upon heating the powder mixture of BaTiO$_3$, Bi$_2$O$_3$ and Nb$_2$O$_5$, was confirmed by endothermic and exothermic peaks in DTA, as shown in Fig. 40. On the other hand, no apparent peaks were observed in DTA during heating pure BaTiO$_3$ (Fig. 41). In the 0.03 and 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped BaTiO$_3$, the DTA curves showed different peaks. However, the exact reason is not clear.

XRD was employed to determine the phases formed during reaction between BaTiO$_3$, Bi$_2$O$_3$ and Nb$_2$O$_5$ during sintering. Before heating, peaks originating from BaTiO$_3$, Bi$_2$O$_3$ or Nb$_2$O$_5$ were easily identified in the XRD pattern, as shown in Fig. 42. After heating the powder mixture to 900°C and air quenching additional peaks (indicated by *) as well as the BaTiO$_3$ were observed, Fig. 43.
Fig. 39. EDS spectrum from reacted layer.
Fig. 40. DTA of BaTiO₃ with 0.03 and 0.05 mol (Bi₂O₃+Nb₂O₅).
Fig. 41. DTA of pure BaTiO₃.
Fig. 42. XRD of 0.05 mol Bi$_2$O$_3$ and Nb$_2$O$_5$ doped starting powder. Bi=Bi$_2$O$_3$, Nb=Nb$_2$O$_5$, BT=BaTiO$_3$.

Fig. 43. XRD of 0.05 mol doped sample heated and air quenched at 900°C.
Those extra peaks could not be attributed to Bi$_2$O$_3$, Nb$_2$O$_5$ or BiNbO$_4$. Similarly, extra peaks were also observed in samples heated and air quenched at 1050°C, 1075°C or 1100°C (Fig. 44), and these extra peaks were also neither from the initial material nor from BiNbO$_4$.

To determine the reaction products giving rise to these extra peaks BaTiO$_3$ with 10, 15 or 25 mol% (Bi$_2$O$_3$ + Nb$_2$O$_5$) was fired at 1150°C for 100hrs. However, the XRD results of those samples, given in appendix IV, were complex and the large number of peaks in the XRD patterns made phase identification very difficult. Moreover, the XRD patterns of different compositions showed the reaction products depended on the dopant concentration. Therefore, the attempt to understand the reactions occurring by correlating the XRD peaks in samples with higher amount of dopants was not successful.

Even though the reactions involved in the system containing BaTiO$_3$, Bi$_2$O$_3$ and Nb$_2$O$_5$ were not determined, the reactions between Bi$_2$O$_3$ and Nb$_2$O$_5$, and between 0.1 mol Bi$_2$O$_3$ and BaTiO$_3$ were better understood. It was found that after firing at 1100°C for 10 minutes Bi$_2$O$_3$ reacted with Nb$_2$O$_5$ and formed BiNbO$_4$. Also, when BaTiO$_3$ was surrounded by a powder mixture of Bi$_2$O$_3$ and Nb$_2$O$_5$, BaTiO$_3$ did not react with the surrounding powder which formed BiNbO$_4$ after firing at 1150°C for 2 hrs. An XRD pattern for BiNbO$_4$, the reaction product, is given in Fig. 45. From these observations, it seems that Bi$_2$O$_3$ can easily and preferably react with Nb$_2$O$_5$ and form stable BiNbO$_4$. 
Fig. 44. XRD of (a) 1050, (b) 1075 and (c) 1100°C air quenched samples.
Fig. 45. XRD of reaction product, BiNbO$_4$. 
When the sample containing 0.1 mol. Bi₂O₃ was fired at 1150°C for 100 hrs., only BaTiO₃ peaks were observed. No Bi₂O₃ peaks nor any other peaks were detected. This observation can be explained as being due to the evaporation of Bi₂O₃ or/and the amount of reaction product was very small.

Pure BaTiO₃ fired at 1200°C for 2 hr. and BaTiO₃ with 0.03 or 0.05 mol dopants fired at 1150°C for 100 hrs. were also studied by XRD, as shown in Fig. 46 and 47. From Fig. 46, it can be seen that small extra peaks were observed in the 0.05 mol doped sample, but not in 0.03 mol doped sample. Moreover, by examining the high angle XRD pattern, the crystal structure of doped samples was seen to have changed from tetragonal to cubic (Fig. 47). The structure transformation was confirmed by the lack of splitting of peaks from planes having the same $h^2+k^2+l^2$. For example, 114, 411, 303 and 330 were separate peaks in tetragonal pure BaTiO₃, but are combined into a single in the doped sample, which showed a cubic structure. Splitting of the high angle peaks, such as 411+113, was due to $K_1$ and $K_2$ radiations, and the lattice parameters of 0.03 and 0.05 mol doped samples were calculated as 4.0146 and 4.0160 Å respectively and the deviation of this measurement was less than 0.1%.
Fig. 46. XRD of (a) 0.03 mol and (b) 0.05 mol Bi and Nb doped BaTiO₃ sintered at 1150°C for 100 hrs.
Fig. 47. High-angle XRD of (a) pure BaTiO₃, (b) 0.03 mol doped and (c) 0.05 mol doped BaTiO₃ samples.
B. Dielectric Properties

The dielectric properties of these Bi and Nb doped materials are of particular interest since the correlation between dielectric properties and microstructure is one of the main objectives of this study. For samples containing 0.05 or 0.03 mol. (Bi$_2$O$_3$ + Nb$_2$O$_5$) with different heat treatments, the relative dielectric constant, $k'$, was measured at temperatures from -55°C to 125°C at 1 KHz. In addition, the variation of dielectric constant as a function of test temperature was indicated by $\Delta k'/k'(25^\circ C)$, where $\Delta k'$ was the difference between the relative dielectric constant at a certain test temperature ($k'(T)$) and the relative dielectric constant at 25°C ($k'(25^\circ C)$), i.e. $\Delta k' = k'(T) - k'(25^\circ C)$. The measured results are shown in Appendices (V and VI) and Figures 48 to 53.

The results show that temperature-stable dielectric materials are found at short sintering times (less than 1 hr.) or lower sintering temperatures (1100°C). Longer sintering time (2 hrs.) or higher sintering temperature (1200°C) deteriorate the temperature stability and decrease the dielectric constant. Furthermore, an increase in $k'$ at 125°C was observed in samples sintered for less than 1 hour.

Samples with different amount of dopants showed similar dielectric character, but the 0.03 mol doped samples had a higher dielectric constant. In addition, samples with lower dopant contents showed less variation of $k'$ over the test temperature.
B. 1. Samples with 0.05 mol dopants sintered at 1100°C

The dielectric constant (k') and the variation of dielectric constant (Δk'/k') of the sample containing 0.05 mol. dopants fired at 1100°C are illustrated in Fig. 48. The highest dielectric constant (1042) was measured in the sample fired for 0.5 hr., and this particular sample showed very good temperature-stability, where Δk'/k' (25°C) ≤ ±3.1%. Temperature-stability was also observed in the 1 hr. fired sample, but the dielectric constant was a little lower (863). For these 1100°C fired samples the dissipation factor, tan δ, at 25°C is around 0.01. Higher tan δ was observed at high and low temperatures (-55 and 125°C), and 4 hrs. sintered sample had a higher dissipation factor (see Appendix V).

For the sample fired for 4 hrs., the variation of relative dielectric constant was increased (Δk'/k' (25°C) ≤ ±12.5%), and higher k' (1001) was measured at -55 and -35°C. When the measuring temperature was raised above 25°C, the relative dielectric constant of the sample sintered for 4 hr. steadily decreased and reached a minimum at 105°C (782). After 105°C, k' again increased.

From the curve of Δk'/k' (25°C) vs temperature, the variation of k' in the high temperature region (65-125°C) was clear. In all samples tested (0.5, 1 and 4 hrs.) an increase of k' at 125°C was observed and a minimum of k' occurred at -85 to 105°C. Moreover, the variation of k' increased with sintering time and the most stable sample was that fired for 0.5 hr.
Fig. 48. Dielectric property of 0.05 mol doped samples sintered at 1100°C.
B. 2. Samples with 0.05 mol dopants sintered at 1150°C

When the sintering temperature was raised to 1150°C, the variation of \(k'\) significantly increased, as shown in Fig. 49 and 50. Similar to samples fired at 1100°C, the gradient of the \(\Delta k'/k'(25°C)\) vs temperature curve increased with sintering time and after 10 hrs. sintering the \(\Delta k'/k'(25°C)\) curve was linear. Sintering time also affected the dielectric constant. In general, at a certain test temperature, the dielectric constant steadily decreased with sintering time. At 25°C, the dissipation factor of these 1150°C sintered samples is always less than 0.002. Higher \(\tan\delta\) was also observed at 125 and -55°C. However, due to the variation of \(\tan\delta\) values it is difficult to generalize a rule to describe the effect of sintering time on it.

For BaTiO\(_3\) with 0.05 mol dopants fired at 1150°C, the most dielectric temperature-stable sample was one sintered for 0.5 hr. (\(\Delta k'/k'(25°C)\leq\pm8.2\%\)), Fig. 49, and an increase in \(k'\) at 125°C was observed. When the test temperature dropped below 105°C, \(k'\) increased with a decrease in temperature. For the samples sintered for longer time (1 hr. or more), the highest relative dielectric constant was always measured at -55°C and \(k'\) steadily decreased with increasing test temperature.

The effect of sintering temperature was important in samples containing 0.05 mol. dopants. In Fig. 51, the dielectric properties of samples sintered for 1 hr. at 1100, 1150 or 1200°C are compared.
Fig. 49. Dielectric property of 0.05 mol doped samples sintered at 1150°C for 0.5 to 10 hrs.
Fig. 50. Dielectric property of 0.05 mol doped samples sintered at 1150°C for 10 to 40 hrs.
Fig. 51. Effect of sintering temperature on dielectric property.
Temperature-stability clearly deteriorated with increasing sintering temperature. Furthermore, the dielectric constant also decreased with increased sintering temperature.

B. 3. Samples with 0.03 mol dopants sintered at 1150°C

For all tested samples the highest relative dielectric constant at 25°C was 1200, measured in the sample with 0.03 mol dopants fired at 1150°C for 0.5 hr. Generally the 0.03 mol doped samples had a higher dielectric constant and a smaller temperature variation than those with 0.05 mol dopants, Fig. 52 and 53. However, the variation of $k'$ with test temperature was analogous to that of the 0.05 mol doped samples. Longer sintering time decreased the dielectric temperature-stability and increased the variation of $k'$ over the test temperatures (-55 to 125°C), as illustrated in Fig. 43. Similar to 0.05 mol doped samples the tanδ at 25°C of all these samples is less than 0.01, and showed a higher value at -55 and 125°C.

In the 0.03 mol doped samples, the most temperature stable one was fired for 0.5 hr., and an increase in $k'$ at 125°C was observed for samples fired for 0.5 and 1 hr. (Fig. 52). In addition, $k'$ was increased by decreasing the test temperature when below 85°C.
Fig. 52. Dielectric property of 0.03 mol doped samples sintered at 1150°C.
Fig. 53. Effect of composition on dielectric property.
C. Microstructural Investigation

In this section sintered samples with different dopant contents were examined with a transmission electron microscope (TEM). In general, the characteristic core-shell structure was observed in Bi$_2$O$_3$ and Nb$_2$O$_5$ doped samples. However, such a core-shell structure was eliminated by longer sintering time (20 hrs.) at 1150°C. In samples doped only with Bi$_2$O$_3$, the core-shell structure was not observed. Domain fringes which extended to grain boundaries were clearly observed and a Bi-rich second phase was detected at grain corners and along the boundaries.

C. 1. Bi$_2$O$_3$ and Nb$_2$O$_5$ doped BaTiO$_3$ sintered at 1100°C

In samples sintered at 1100°C for 0.5 to 2 hrs. and doped with 0.03 or 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$), the core-shell structure was observed in numerous grains, and typical TEM bright-field images of samples containing 0.05 or 0.03 mol dopants are shown in Fig. 54 and 55. The observed core-shell structure is clearly illustrated by the appearance of ferroelectric domain fringes in the grain core but no domain fringes are visible in the shell. In addition, no clear boundary between the core and shell was noticed.

The formation of a core-shell structure in Bi and Nb doped samples was not restricted to grains of certain size ranges. In the
Fig. 54. Grains with a core-shell structure in 0.05 mol (Bi$_2$O$_3$ +Nb$_2$O$_5$) doped BaTiO$_3$ sintered at 1100°C for 1 hr.
Fig. 55. Grains with a core-shell structure in 0.03 mol (Bi$_2$O$_3$ + Nb$_2$O$_5$) doped BaTiO$_3$ sintered at 1100°C for 2 hrs.
sample with 5 wt% large BaTiO₃ particles and sintered at 1100°C 0.5 hr., the core-shell structure was observed in grains of different sizes. As shown in Fig. 56, a clear core-shell structure was observed in small grains, 0.2-0.3 um, and a large grain, 4 um. Apparently, the initial BaTiO₃ particle size does not affect the formation of the core-shell structure. However, the thickness of grain shells in small and large grains was dramatically different. In a small grain, the shell thickness could be less than 0.03 um, but in a large grain the thickness was more than 1 um. These observations indicated that even though the core-shell structure was homogeneously formed throughout the sample and in grains of different sizes, the growth rate of the grain shell's thickness was quite different from one grain to the other.

For all the Bi₂O₃ and Nb₂O₅ doped and 1100°C sintered samples the grain size was measured and the average grain sizes of samples with different treatments are listed in Table I. The deviation of the average grain sizes is about 10%. The number of count, mean and standard distribution deviation of each sample's grain size measurement are listed in Appendix VII (A). Slight grain growth with sintering time was observed in both 0.03 and 0.05 mol doped and 1100°C sintered samples, and the 0.05 mol doped samples showed larger grain sizes.

Besides the average grain size, the average sizes of core and grain in grains showing a clear core-shell structure were also measured and listed in Table II; the number of count, mean and
Fig. 56. The core-shell structure in (a) small grains (arrowed) and (b) a large grain. This specimen contained 5 wt% large BaTiO$_3$ particles and sintered at 1100°C for 0.5 hr.
Table 1
Average Grain Size of Bi$_2$O$_3$ and Nb$_2$O$_5$ Doped BaTiO$_3$
Sintered at 1100°C

<table>
<thead>
<tr>
<th>Sintering Time</th>
<th>0.5 hr.</th>
<th>1 hr.</th>
<th>2 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03 mol</td>
<td>0.43 μm</td>
<td>0.45 μm</td>
<td>0.55 μm</td>
</tr>
<tr>
<td>0.05 mol</td>
<td>0.51 μm</td>
<td>0.52 μm</td>
<td>x</td>
</tr>
</tbody>
</table>

Table 2
Average Core and Grain Size of Grains with Core-Shell Structure
in Bi$_2$O$_3$ and Nb$_2$O$_5$ doped BaTiO$_3$ sintered at 1100°C

<table>
<thead>
<tr>
<th>Sintering Time</th>
<th>0.5 hr.</th>
<th>1 hr.</th>
<th>2 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03 mol</td>
<td>0.49 μm</td>
<td>0.61 μm</td>
<td>0.67 μm</td>
</tr>
<tr>
<td>Core Size</td>
<td>0.38 μm</td>
<td>0.44 μm</td>
<td>0.47 μm</td>
</tr>
<tr>
<td>Core Vol. %</td>
<td>46.6</td>
<td>37.5</td>
<td>34.5</td>
</tr>
<tr>
<td>0.05 mol</td>
<td>0.63 μm</td>
<td>0.71 μm</td>
<td></td>
</tr>
<tr>
<td>Core Size</td>
<td>0.48 μm</td>
<td>0.50 μm</td>
<td></td>
</tr>
<tr>
<td>Core Vol. %</td>
<td>44.2</td>
<td>34.9</td>
<td></td>
</tr>
</tbody>
</table>
standard distribution deviation are shown in Appendix VII (B). In addition, the volume fraction of grain cores, \((\text{core size})^3/(\text{grain size})^3\), was calculated and listed. Generally, the average grain size of grains showing a clear core-shell structure was larger than the average grain size of all the measured grains; this difference was mainly because in some grains, especially the smaller ones, the core-shell structure was not easy to observe.

For grains showing a clear core-shell structure, an increase of the average grain size with sintering time is easily detected in both 0.03 and 0.05 mol doped samples, and the volume fraction of grain cores steadily decreased with sintering time. On the other hand, the average size of grain cores was slightly increased with time. Even though the core size increase was small and less than the measurement deviation (about 0.08 \(\mu\text{m}\)), this observation is still interesting and will be discussed later.

C. 2. 0.05 mol \((\text{Bi}_2\text{O}_3+\text{Nb}_2\text{O}_5)\) doped \(\text{BaTiO}_3\) sintered at 1150°C

Since sintering time was an important factor in affecting the microstructure development, 0.05 mol \((\text{Bi}_2\text{O}_3+\text{Nb}_2\text{O}_5)\) doped and 1150°C sintered samples were then studied after sintering for 0.5 to 40 hrs. In samples with 0.05 mol dopants sintered at 1150°C, the change of microstructure as a function of sintering time was evident, as shown in Fig. 57 and 58. In the 0.5 and 2 hr. sintered samples, large core areas were observed and these grain cores were not always
Fig. 57. Microstructures of 0.05 mol doped BaTiO$_3$ sintered at 1150°C for (a) 0.5 hr., (b) 2 hrs., (c) 4 hrs., and (d) 10 hrs.
Fig. 58. Microstructures of 0.05 mol doped BaTiO$_3$ sintered at 1150°C for (a) 20 hrs., and (b) 40 hrs.
at grain centers. The region of ferroelectric grain cores then gradually decreased with sintering time. After 20 hrs., no ferroelectric grain core was visible and all the grains became homogeneously non-ferroelectric at the examining temperature (25°C). In addition, grain growth with sintering time was observed. In the 0.5 hr. sintered sample the average grain size was about 0.4 um. After 40 hrs. sintering, large grains (about 6 um) were observed, Fig. 58. Some fringes were noticed in the grains of samples sintered for 20 and 40 hrs. However, the reason for these fringes is not clear.

In all samples, clear thickness fringes at grain boundaries were observed. No second phase was noticed on the boundaries or at the grain corners. In addition, in samples fired for long times, no second phase particle or precipitate was detected inside the homogeneous non-ferroelectric grains. In this study, a Nb- and Bi-rich phase was observed and will be described in this chapter section F. This dopant-rich phase, however, was always agglomerated and localized in certain regions and was not observed on the boundaries or inside the grains.

As with the 1100°C fired samples, size measurements were conducted on the 0.05 mol doped and 1150°C sintered samples; the volume fraction of ferroelectric grain cores was also calculated. The measured and calculated results are shown in Table III and IV,
the number of counts, means and standard distribution deviations are listed in Appendix VIII. The deviation of the measured average sizes is around 0.2-0.4 μm. As illustrated in Table III, grain growth did occur in these 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped and 1150°C sintered samples. The average grain size increased from 0.57 μm (0.5 hr. sample) to 3.89 μm (40 hrs. sample). Even though the growth rate was slow, grain growth was still evident in the microstructures and grain size measurements.

In Table IV, the average sizes of grains and cores in grains with a clear core-shell structure are listed. Since no core-shell structure was observed in 20 and 40 hrs. sintered samples, no such measurement was conducted in these two samples. Furthermore, in the 10 hrs. sample (with a * mark in Table IV), very few grain cores (3) were observed. Similar to the 1100°C sintered samples, the average grain size of grains showing a clear core-shell structure was 20 to 35% larger than the overall average grain size. In addition, the volume fraction of grain cores steadily decreased with sintering time, from 37.1% in the 0.5 hr. sample to less than 1.3% in the 10 hr. sample.

Associated with the increase of average grain size with sintering time, a slight increase of core size was also noticed, from 0.51 μm in 0.5 hr. sample to 0.56 μm in 4 hr. sample, and the deviation was about 0.1 μm. In the 10 hr. sample, however, the average core size decreased to 0.5 μm.
### Table 3

Average Grain Size of 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped BaTiO$_3$
Sintered at 1150°C

<table>
<thead>
<tr>
<th>Sintering Time</th>
<th>0.5 hr.</th>
<th>2 hrs.</th>
<th>4 hrs.</th>
<th>10 hrs.</th>
<th>20 hrs.</th>
<th>40 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Size</td>
<td>0.57µm</td>
<td>0.91µm</td>
<td>1.36µm</td>
<td>1.55µm</td>
<td>2.19µm</td>
<td>3.89µm</td>
</tr>
</tbody>
</table>

### Table 4

Average Core and Grain Size of Grains with Core-Shell Structure
in 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped BaTiO$_3$ sintered at 1150°C

<table>
<thead>
<tr>
<th>Sintering Time</th>
<th>0.5 hr.</th>
<th>2 hr.</th>
<th>4 hr.</th>
<th>10 hrs.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Size</td>
<td>0.71 µm</td>
<td>0.92 µm</td>
<td>1.63 µm</td>
<td>2.1 µm</td>
</tr>
<tr>
<td>Core Size</td>
<td>0.51 µm</td>
<td>0.53 µm</td>
<td>0.56 µm</td>
<td>0.5 µm</td>
</tr>
<tr>
<td>Core Vol. %</td>
<td>37.1</td>
<td>19.1</td>
<td>4.05</td>
<td>1.3</td>
</tr>
</tbody>
</table>
C. 3. \( \text{Bi}_2\text{O}_3 \) doped \( \text{BaTiO}_3 \)

In samples doped only with \( \text{Bi}_2\text{O}_3 \), the microstructures were dramatically different. After sintering at 1150°C for 1 or 40 hrs., a core-shell structure was not formed, as shown in Fig. 59. Moreover, in the singly-doped (\( \text{Bi}_2\text{O}_3 \)) samples, grain growth was inhibited. The average grain size of 1 hr. sintered sample was 0.39 um and the size of 40 hrs sample was only 0.41 um. In a sample sintered for 40 hrs., ferroelectric domain fringes were obvious, Fig. 59 (b), and those fringes extended throughout the grains at the examining temperature (25°C). Apparently no non-ferroelectric region was developed and no core-shell structure was formed in \( \text{Bi}_2\text{O}_3 \) doped samples.

By comparing the TEM images of samples sintered at 1150°C 40 hrs. but containing different dopants, singly doped (\( \text{Bi}_2\text{O}_3 \)) or binary doped (\( \text{Bi}_2\text{O}_3+\text{Nb}_2\text{O}_5 \)), the effect of dopants on microstructure was even clearer, as shown in Fig. 60. In the Bi and Nb doped sample, homogeneous non-ferroelectric grains (3.89 um) were formed and slight grain growth occurred. On the other hand, ferroelectric grains (0.41 um) without grain growth were observed in the sample doped only with \( \text{Bi}_2\text{O}_3 \).

Besides the difference inside the grains, these samples also differ at the grain boundaries. In Bi and Nb doped samples, clear boundary fringes were observed and no second phase was detected.
Fig. 59. Microstructures of 0.1 mol Bi₂O₃ doped BaTiO₃ sintered at 1150°C for (a) 1 hr. and (b) 40 hrs.
Fig. 60. Microstructures of (a) 0.1 mol Bi₂O₃ and (b) 0.05 mol (Bi₂O₃+Nb₂O₅) doped BaTiO₃ sintered at 1150°C 40 hrs.
However, in 0.1 mol Bi$_2$O$_3$ doped samples, a 2nd phase was clearly observed, Fig 61, and this 2nd phase either accumulated at grain junctions or spread along grain boundaries. It has been confirmed by electron diffraction in TEM that the 2nd phase in the Bi doped sample had a crystalline structure, as shown in Fig. 53, but no detailed analysis of lattice spacings was carried out. In addition, this second phase showed a very high Bi content in the EDS spectrum (Fig. 62 (c)).

In the sample doped with 0.1 mol Bi$_2$O$_3$ and fired at 1150°C for 40 hrs., EDS analysis was not only performed on the 2nd phase but also on grain boundaries and inside grains. On the boundary, as shown in Fig. 63, instead of clear boundary fringes a dark line was observed and Bi was detected. Moreover, a small amount of Bi was also noticed inside the grain.

The observations in the 0.1 mol Bi$_2$O$_3$ doped samples indicated that Bi$_2$O$_3$ reacted with BaTiO$_3$ and formed a second phase during sintering. This second phase was located at the grain corners or spread along the boundaries suggesting it was liquid at the sintering temperature. The lack of grain growth could then possibly be attributed to the appearance of the 2nd phase. In the 40 hrs. sintered sample, little Bi was found to diffuse into BaTiO$_3$ grains. However, the existence of Bi did not change those grains from the ferroelectric to the non-ferroelectric state at 25°C and no core-shell structure was formed.
Fig. 61. Second phase (arrowed) in 0.1 mol Bi₂O₃ doped BaTiO₃ sintered at 1150°C for (a) 1 hr. and (b) 40 hrs.
Fig. 62. TEM (a) BF image, (b) diffraction pattern and (c) EDS spectrum of the second phase in 0.1 mol Bi$_2$O$_3$ doped BaTiO$_3$ sintered at 1150$^\circ$C 40 hrs.
Fig. 63. EDS spectra of a second phase, the grain boundary (G.B.) and inside a grain (GR). TEM image showing the analyzed area.
D. Grains with a Core-Shell Structure

Some large grains with a clear core-shell structure were studied in detail. Electron diffraction patterns of the grain core and grain shell were carefully examined and the planar defects within a grain were also analyzed. In addition, the distribution of Bi and Nb across grains with a core-shell structure was investigated by EDS semi-quantitatively. The effect of dopants, Bi and Nb, on the ferroelectric to non-ferroelectric transformation temperature was also examined.

D. 1. Grain core and grain shell

In Fig. 64 and 65, grains with a core-shell structure are illustrated. Two distinct regions, core and shell, show very different contrast in TEM bright field images. Within the grain core closely-spaced fringes were observed, while the shell showed relatively homogeneous contrast with some planar defect fringes.

Many planar defects, such as domain boundaries, stacking faults, anti-phase boundaries and twins, may give rise to fringes in TEM images. Therefore, an experiment to differentiate the planar defects in the grain core and grain shell was performed. A 1150°C 0.5 hr. sintered specimen was examined in TEM by using a temperature-controlling specimen holder, which controlled the specimen's temperature from -174 to 150°C. Since BaTiO$_3$ changes from
Fig. 64. TEM BF image of a grain with a core-shell structure. This specimen was doped with 0.05 mol dopants and sintered at 1150°C 2 hrs. (dislocations on the boundary are arrowed).
Fig. 65. TEM BF image of a grain with a core-shell structure. This specimen was doped with 0.05 mol dopants and sintered at 1150°C for 0.5 hr.
ferroelectric to paraelectric at 130°C (the Curie temperature, Tc), ferroelectric domain boundaries should disappear after the specimen's temperature is raised above the Curie temperature. Therefore, by comparing the images below and above the Curie temperature, we can easily differentiate the fringes caused by domain boundaries or by the other planar defects.

In Fig. 66, dark-field images of a grain at 30 and 132°C were illustrated, and a clear difference between the images at different temperatures is apparent. At 30°C, the core-shell structure was clearly observed, but at 132°C fringes in the grain core disappeared and fringes in the grain shell remained unchanged. Consequently, it was confirmed that the fringes in the grain core were caused by domain boundaries and the core area was ferroelectric at room temperature. At 132°C, the grain core changed from ferroelectric to the non-ferroelectric state. Associated with this change, the domain boundaries disappeared, and the disappearance of the domain boundaries was illustrated by the disappearance of the fringes in the core.

The fringes in the grain shell, on the other hand, were not affected by temperature. This observation then indicated that the fringes in grain shell were not caused by domain boundaries but by other planar defects, and the grain shell was non-ferroelectric at the investigation temperatures (30 to 132°C).
Fig. 66. TEM DF images (g-011) of a grain examined at (a) 30°C and (b) 132°C. This specimen was doped with 0.05 mol dopants and sintered at 1150°C 0.5 hr.
It could be seen from Fig. 64, 65 and 66 that the domain fringes in the core did not penetrate into the shell region, and the planar defects in the shell also stopped when they met the grain core. In addition, no clear boundary was observed between core and shell. Sharp grain corners and clear boundary fringes were noticed; some dislocations were observed on grain boundaries (arrowed in Fig. 64). Furthermore, no second phase or precipitate was detected on the boundaries or in the grain shell.

Besides fringes, TEM electron diffraction patterns of the grain core and grain shell were also compared (Fig. 67). Splitting of diffraction spots was observed in the diffraction pattern of the grain core, but the diffraction spots from the shell were not split. The splitting of diffraction spots in the core was caused by slight orientation differences between ferroelectric domains. Owing to the non-ferroelectric structure in the shell, no splitting of the diffraction spots occurred.

Apart from the spot splitting in the core pattern, the diffraction patterns of core and shell were almost identical. No measurable difference in the reciprocal lattice spacing was observed. The electron diffraction patterns were perfectly continuous from one to the other. The continuity of the electron diffraction pattern indicated the coherence between the core and the shell, and indeed no sharp boundary was observed between them.
Fig. 67. TEM electron diffraction patterns of (a) the grain core and (b) the grain shell. Note the splitting of spots (arrowed) in (a) but not in (b).
D. 2. Planar defects in grain shell

In the previous section it was confirmed that the fringes from planar defects in the grain shells were not caused by ferroelectric domain boundaries since they were unaffected by raising the temperature above \( T_c \). The planar defects in the grain shells were associated with the core-shell structure. Usually the planar defects were observed in large grains (>1\( \mu m \)) and in samples sintered at 1150\( ^\circ \)C for less than 20 hrs. In samples sintered for 20 hrs. or more, the core areas were completely eliminated and no planar defects were ever observed.

The planar defects in the shell usually surrounded the grain core and were oriented in certain directions, as shown in Fig. 64, 65 and 68. In one of the grains investigated, three sets of parallel planar defects were observed and indexed as A, B and C in Fig. 69. This particular grain was examined at the [111] zone axis and tilted to obtain a variety of two-beam conditions, (i.e. a single set of planes at the Bragg condition). For this grain, the reflecting planes were set at (10\( \overline{1} \)), (0\( \overline{1} \)1) or (\( \overline{1} \)10) respectively. While the reflecting planes were (10\( \overline{1} \)), i.e. \( g=10\overline{1} \), the fringes indexed as B became invisible, as illustrated in Fig. 70 (a). Similarly with \( g=0\overline{1}1 \) or \( \overline{1}10 \), Fig. 70 (b) and (c), A or C fringes disappeared respectively. This observation meant that the displacement vector of the planar defects, \( \mathbf{R} \), was perpendicular to \( g \) and \( \mathbf{R} \cdot g = 0 \). Also, it was found that in the grain (shown in Fig.
65) one set of planar defects in the shell was perpendicular to [111], and the dark-field image of the grain when $g = \overline{111}$ is shown in Fig. 71. These observations then indicate the planar defects in the shell lie on (111) planes and the possible $R$ is $1/3 <111>$ or $1/6 <112>$.

In addition to these observations, TEM bright-field (BF) and dark-field (DF) images of the planar defects were also compared. As shown in Fig. 72, the bright and dark fringes were symmetrical in the BF image but were asymmetrical in the DF image. Since boundaries (e.g. BaTiO$_3$ 90° domain boundaries) show inverse behavior (i.e. asymmetrical in BF and symmetrical in DF), and the fringes of boundaries (e.g. antiphase domain boundaries) are symmetrical in both BF and DF images, these two types of boundaries can be ruled out. Therefore, the only possible origin of the fringes in the shell were fringes from stacking faults, twins, or precipitates. If precipitate planes were stably formed during sintering and cause the fringes in the shell, longer sintering time should lead to the growth of larger precipitate particles. However, longer sintering time eliminated the planar defects in the shell and no precipitates were ever observed in TEM images or detected using EDS. If the fringes were from twin boundaries they would show spot splitting or different intensities in diffraction patterns. This was not observed. Consequently, the planar defects in the shell are most likely to be stacking faults. No detailed analysis of the nature (i.e. intrinsic or extrinsic) of the stacking faults was attempted.
Fig. 68. Planar defects in the grain shell.
Fig. 69. TEM (a) BF image and (b) diffraction pattern of a grain with three sets of planar defects (A, B and C) in the grain shell.
Fig. 70. TEM DF images of a grain with three sets of planar defects (A, B and C) when (a) $g = \overline{101}$, (b) $g = \overline{011}$ and (c) $g = \overline{110}$. 
Fig. 71. TEM DF image of a grain (g=111) showing one of the planar defects in the shell perpendicular to <111>.
Fig. 72. TEM (a) BF and (b) DF images of the planar defects in the shell.
D. 3. Chemical analysis

Apart from the observed ferroelectric domains in the grain core, the major difference between the core and shell of a grain was composition. EDS microanalysis of a grain core in a sample containing 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) and sintered for 0.5 hr. revealed that there were practically no additives in the core, as shown in Fig. 73 (a). On the other hand, the dopants, Bi and Nb, concentrated themselves in the shell, Fig. 73 (b).

Since the Ba(Lα) and Ti(Kα) peaks overlap and cannot be distinguished in an EDS spectrum, these two peaks combine and form the main peak. In addition, the Ba(Lβ) peak also overlaps with the Ti(Kβ) peak. Therefore, to quantify the relative mole ratio of Ba to Ti was difficult. However, the relative amount of Bi or Nb to Ba+Ti could be determined by the ratio of the counts in Bi(Lα) peak or Nb(Kα) peak to the counts in the main peak (Ba(Lα)+Ti(Kα)). The relative distribution of the dopants, Bi and Nb, within a grain could then be determined by comparing the ratios of Bi/Ba+Ti and Nb/Ba+Ti across the grain.

As shown in Fig. 74, a grain in the sample sintered at 1150°C for 0.5 hr. was examined in the TEM (at -174°C to avoid contamination), and EDS point analysis was conducted across the grain core and shell. The analyzed length of this particular grain was 1.14 μm and the size of core at -174°C was 0.7 μm. The chemical
Fig. 73. EDS spectra of (a) the grain core and (b) the grain shell in the specimen doped with 0.05 mol dopants and sintered at 1150°C for 2 hrs.
Fig. 74. Bi and Nb concentration profiles across a grain in the specimen with 0.05 mol dopants and sintered at 1150°C for 0.5 hr.
analysis results revealed a clear compositional difference between the core and shell. The profiles of Bi/Ba+Ti and Nb/Ba+Ti count ratios across the grain indicated a higher Bi and Nb concentration in the shell and very low Bi and Nb content in the core. Additionally, the grain core was not at the center of the grain, and the Bi and Nb concentration profiles were not symmetric. Furthermore, the concentrations of Bi and Nb were shown to gradually decrease from the shell toward the core center. The gradients of the profiles are shallow with no sharp compositional difference at the core and shell boundary.

Similar EDS point analysis was also performed at -174°C on specimens sintered at 1150°C for 4 hrs. and 10 hrs., as shown in Fig. 75 and 76. From the examined grains, the results illustrated that in both the 4 and 10 hrs. sample higher Bi and Nb contents were detected in the shells. On the other hand, the concentration of dopants in the cores increased with sintering time. Asymmetric and shallow concentration profiles were observed in these two grains, and no sharp compositional difference was detected at the core-shell boundary.

By comparing the dopant concentration profiles of samples sintered at 1150°C for different times (0.5, 4 and 10 hrs.), Fig. 77, the general effect of sintering time on dopant distribution
Fig. 75. Bi and Nb concentration profiles across a grain in the specimen with 0.05 mol dopants and sintered at 1150°C for 4 hrs.
Fig. 76. Bi and Nb concentration profiles across a grain in the specimen with 0.05 mol dopants and sintered at 1150°C for 10 hrs.
Fig. 77. Bi and Nb concentration profiles across grains sintered at 1150°C for (a) 0.5 hr., (b) 4 hrs. and (c) 10 hrs.
inside a grain can be ascertained. With longer sintering time, the content of dopants in the grain core was increased and the distribution of dopants was more homogeneous. The ratio of Bi(Lα) peak to Ba(Lα)+Ti(Kα) peak at the core center increased from 0.014 (0.5 hr. sample) to 0.048 (10 hrs. sample). The ratio of Nb(Kα) to Ba(Lα)+Ti(Kα) at the core center also increased from 0.006 (0.5 hr.) to 0.020 (10 hrs.). On the other hand, ratios of Bi and Nb to Ba+Ti in the shell slightly decreased with sintering time. Bi/Ba+Ti changed from 0.069 (0.5 hr.) to 0.06 (10 hrs.), and Nb/Ba+Ti from 0.04 to 0.03. Even though the content of Bi and Nb in the grain shell slightly decreased with sintering time, by comparing the area under the Bi and Nb distribution profiles the total amount of dopants inside a grain was evidently increased. In addition, in all grains investigated, the shallow concentration profiles of Bi and Nb were always essentially parallel to each other.

At the core shell boundary, Bi/Ba+Nb and Nb/Ba+Ti ratios were relatively constant at the examining temperature, -174°C. Bi/Ba+Ti was about 0.043-0.047 and Nb/Ba+Ti was around 0.02-0.025. When enough Bi and Nb (Bi/Ba+Ti > 0.047 and Nb/Ba+Ti > 0.025) were incorporated into the BaTiO₃ lattice, a non-ferroelectric region was formed. Otherwise, the ferroelectric state was retained.
D. 4. Ferroelectric to non-ferroelectric transformation

The results described above show that ferroelectric BaTiO$_3$ domains transform to the non-ferroelectric state by incorporation of Bi and Nb. In addition, the concentration of dopants gradually decrease from the shell toward the center of the grain core. At -174°C, when the Bi/Ba+Ti and Nb/Ba+Ti ratios were larger than 0.047 and 0.025 respectively, a non-ferroelectric grain shell was developed. Moreover, the grain core of a BaTiO$_3$ grain was also transformed to the non-ferroelectric state when the temperature was raised above 132°C. In this section, results of the effect of specimen temperature on the transformation from ferroelectric to non-ferroelectric state are presented.

A particular grain in the 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) doped sample sintered at 1150°C for 4 hrs. was examined in the TEM with a temperature-controlling specimen holder. For this grain, the investigation temperature was set between -174°C and 140°C. TEM bright-field images at different temperatures are illustrated in Fig. 78. The change of core size as a function of the specimen temperature is clearly demonstrated. As the temperature increased, the size of the ferroelectric grain core decreased, and at 140°C the whole grain became non-ferroelectric. Since diffusion of dopants is not expected to occur in this temperature range (-174 to 140°C), dopant concentration profiles should not alter and the change of grain core size can be attributed to the examination temperature.
Fig. 78. TEM BF images of a grain sintered at 1150°C 4 hrs. and examined at temperatures from -174 to 140°C.
Fig. 79. TEM BF images of a grain sintered at 1150°C 10 hrs. and examined at temperatures from -174 to 140°C. (grain core is arrowed)
The temperature effect is a function of the Bi and Nb content that resulted from sintering. Higher Bi and Nb content lowered the transformation temperature.

A grain of the sample with 0.05 mol dopants sintered at 1150°C for 10 hrs. was similarly investigated. As shown in Fig. 79, the size of the ferroelectric grain core was also reduced with increased temperature. However, in contrast to the 4 hr. sintered sample, the whole grain core (arrowed in the figures which contained higher Bi and Nb, see Fig. 76) transformed to the non-ferroelectric state at 0°C. Thus the ferroelectric to non-ferroelectric transformation is confirmed to be a function of temperature, and the transformation temperature is shown to depend on dopant concentration.

E. Grain Boundaries

TEM bright-field images of samples with 0.05 mol dopants and sintered at 1150°C are given in Fig. 80, 81 and 82. In all these images, clear grain boundary fringes and sharp grain corners are observed. In addition, many dislocations (Fig. 80 and 81) and boundary ledges (Fig. 82) occur on the boundaries. Furthermore, Fig. 74 and 75 also showed that the ferroelectric core was eliminated, while the grain boundaries remained clean, i.e. no second phase or precipitates were observed on boundaries during sintering.
Fig. 80. Dislocations on grain boundaries of specimens with 0.05 mol dopants and sintered at 1150°C for (a) 0.5 hr. and (b) 2 hrs.
Fig. 81. Dislocations on grain boundaries of specimens with 0.05 mol dopants and sintered at 1150°C for (a) 10 hrs. and (b) 40 hrs.
Fig. 82. Boundary ledges on grain boundaries of specimen sintered at 1150°C for (a) 4 hrs., (b) 4 hrs. and (c) 10 hrs.
EDS point analysis was performed across one grain boundary of the 1150°C 0.5 hr. fired sample, and the results are shown in Fig. 83. During the investigation, the specimen temperature was maintained at -174°C to avoid contamination, and the analysis was conducted in areas where the electron beam was parallel to the grain boundary. The electron beam current was carefully monitored and kept constant. The time to acquire the EDS spectrum was also kept constant. Furthermore, the ratio of Bi(L) peak or Nb(K) peak to Ba(L)+Ti(K) peak was used to demonstrate the dopant concentration across the grain boundary.

In the 0.5 hr. fired sample, higher Bi and Nb content near the grain boundary is illustrated in Fig. 83. The concentration of Bi or Nb showed a maximum at the boundary and gradually decreased toward grain centers. In addition, no evident Bi or Nb-rich layer was observed at the boundary, and the gradient of the profiles was shallow. Both the Bi and Nb profiles were not symmetric about the grain boundary.

A similar analysis was conducted for the sample sintered at 1150°C for 10 hrs. As shown in Fig. 84, both of the profiles of Bi/Ba+Nb and Nb/Ba+Nb are flat. Constant dopant concentration was maintained across the boundary, and no dopant-rich layer was detected.

Fig. 85 is a comparison of the Bi and Nb profiles of 0.5 and 10 hrs. sintered samples. At the grain boundary, the amount of Bi
Fig. 83. Bi and Nb concentration profiles across a grain boundary of the sample with 0.05 mol dopants and sintered at 1150° for 0.5 hr.
Fig. 84. Bi and Nb concentration profiles across a grain boundary of the sample with 0.05 mol dopants and sintered at 1150°C for 10 hrs.
Fig. 85. Bi and Nb concentration profiles across the boundaries of samples sintered for 0.5 and 10 hrs.
and Nb clearly decreased with sintering time. On the other hand, Bi and Nb contents inside the grains greatly increased. Also, in both of the boundary areas examined, no highly dopant-rich layer was detected.

In this research, close attention was paid to grain boundary regions. Especially, the structure and composition on the grain boundaries. In all the specimens investigated, which were doped with 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$) and sintered at 1150$^\circ$C, no second phase or amorphous layer was observed at the grain corners or on the boundaries. In addition, no precipitates were observed. Through EDS microanalysis of the 0.5 hr. sintered sample, Fig. 83, higher Bi and Nb contents were detected near the grain boundaries than inside the grains. However, no evidence for the existence of a dopant-rich layer or phase was found. The increase in dopant content from core to shell to grain boundary was gradual and no sudden increase was found at the grain boundary. After 10 hrs. sintering, the whole system became more chemically homogeneous, and the composition near the grain boundary was the same as that of adjacent grains, Fig. 84.
F. Nb- and Bi-rich phase

Microstructural and chemical analysis has shown that the core-shell structure formed in all samples doped with 0.05 mol\((\text{Bi}_2\text{O}_3+\text{Nb}_2\text{O}_5)\) and sintered at 1150\(^\circ\text{C}\) for 0.5 hr. Higher Bi and Nb contents were detected on the grain boundaries and in grain shells; and the dopant concentration gradually decreased toward the core center. After 10 hrs. sintering at 1150\(^\circ\text{C}\), the total content of Bi and Nb within a grain increased and the core fraction was reduced. The size of a ferroelectric grain core was a function of composition and examination temperature. Although the investigation was conducted at room temperature, the volume of the ferroelectric cores was mainly affected by the distribution and concentration of dopants resulting from sintering and not the examination temperature.

Results show that a longer sintering time made the distribution of Bi and Nb more homogeneous and enriched the Bi and Nb content inside a \(\text{BaTiO}_3\) grain (Fig. 84). In contrast, the concentration of Bi and Nb on the boundaries and in the grain shells did not change much. Also, no Bi- and Nb-rich phase was observed at grain corners or on the boundaries. Therefore, there must be another source supplying the dopants.

In order to help understand the reactions in this doped system, and determine the source supplying Bi and Nb and kinetics of dopant transport, samples heated at 1075 and 1100\(^\circ\text{C}\) were air quenched and examined.
F. 1. 1075°C air quenched sample

This sample was heated to 1075°C at a rate of 10°C/min and then removed from the furnace to air quench. The density was still low, 4.672 g/cm³. Most of the grains were still in the ferroelectric state. Domain fringes extended to the boundaries and the core-shell structure had not yet developed, Fig. 86 (a). However, in some other regions, non-ferroelectric grains were also observed Fig. 86 (b). In those areas, around 2 μm in diameter, non-ferroelectric grains (around 0.4 μm in diameter) collected together.

EDS qualitative analysis was conducted in those non-ferroelectric grains, (labeled as grains 1 to 9) and it was found that Nb and Bi were enriched in those grains with Ba and/or Ti also detected, as shown in Fig. 87. All the grains had the same composition and a typical EDS spectrum is shown in Fig. 87 (b). EDS analysis on neighbouring grains, Fig. 88, revealed little Bi and Nb in grains 10 and 11, which were next to the Nb- and Bi-rich phase. In grains farther away, 12 to 15, no dopants were detected. An electron diffraction pattern and dark-field image prove the Nb- and Bi-rich phase had a crystalline structure, as shown in Fig. 89. However, the lattice spacing and the crystal symmetry of this phase was not analyzed.
Fig. 86. TEM images of (a) ferroelectric grains and (b) non-ferroelectric grains in the 1075°C air quenched and 0.05 mol doped sample.
Fig. 87. TEM image and EDS spectra of Nb- and Bi-rich phase in the 1075°C air quenched and 0.05 mol doped sample.
Fig. 88. TEM image and EDS spectra of grains with different compositions in the 1075°C air quenched and 0.05 mol doped sample.
Fig. 89. TEM (a) DF image and (b) diffraction pattern of a Nb- and Bi-rich phase.
F. 2. 1100°C air quenched sample

In the 1100°C air quenched sample, completely ferroelectric grains, grains with core-shell structure and non-ferroelectric grains were all observed, as shown in Fig. 90. In this sample, grain boundaries were clear and no boundary layer was detected.

EDS analysis was also performed in one area of this specimen and the results are shown in Fig. 91. In the analyzed area, grains of different compositions were observed. Grains 10 and 11, were enriched in Nb and Bi, and the neighbouring grains, 1 to 6, showed high Bi and Nb content. In grains further away, 7 to 9, no dopants were detected. Evidently, regions with different Bi and Nb contents are present. Pure BaTiO₃ was usually found in the grain cores of these samples sintered for short times. Higher Bi plus Nb content was typical of the shell regions or in grains in longer-sintered samples with high dopant content. Grains of this composition had commonly changed to the non-ferroelectric state. The Nb- and Bi-rich phase represented a compound formed during sintering. By comparing the relative Bi and Nb EDS peak heights, the Nb- and Bi-rich phase could easily be distinguished from the BaTiO₃ grains with Bi and Nb in solid solution.

In the 1100°C air quenched sample, EDS point analysis was also conducted in another area, as shown in Fig. 92. In this area the Nb-and Bi-rich phase was not detected and only BaTiO₃ grains
Fig. 90. TEM BF images of 1100°C air quenched and 0.05 mol doped BaTiO$_3$. 
Fig. 91. TEM image and EDS spectra of grains with different compositions in 1100°C air quenched and 0.05 mol doped sample.
Fig. 92. EDS spectra of grain cores (1 and 4), grain shells (2 and 5) and grain boundaries (3 and 6) in the 1100°C air quenched and 0.05 mol doped sample.
were observed. In the grain centers, spot 1 and 4, no dopants were detected. Bi and Nb were noticed in the grain shells, spot 2 and 5, and higher Bi and Nb were detected on the boundaries, 3 and 6. This region was more representative of the general microstructure in the 1100°C quenched sample. Higher Bi and Nb were detected on the boundaries and no dopants in the grain centers.

Evidently, at the early stages of sintering the whole system is chemically inhomogeneous. The Nb and Bi-rich phase is localized in certain areas, and the grains closest to this Nb- and Bi-rich have higher Bi and Nb contents and form a BaTiO₃ solid solution earlier. Grains further away from the Nb, Bi source are still ferroelectric. Higher Bi and Nb were detected on the boundaries and some Bi and Nb had diffused into BaTiO₃ grains.

F. 3. 1150°C 10 hrs. sintered sample

In the 1150°C 10 hrs. sintered sample, most of the grains have transformed to the non-ferroelectric state. These grains are mainly BaTiO₃ with Bi and Nb in solid solution. However, in this particular specimen, the Nb- and Bi-rich phase was also detected, as shown in Fig. 93. Grains 1 to 3 showed enriched Nb and Bi, while the other grains are non-ferroelectric BaTiO₃ solid solution. Clear boundary fringes were noticed and no boundary layer was observed. Fig. 94 is a higher magnification image of the microstructure of
this region. The grains labeled in Fig. 94 were identical to those in Fig. 93. Clear boundary fringes are apparent, and the dopant-rich grain, grain 3, does not penetrate through the boundary between BaTiO$_3$ grains, 4 and 5. In addition, by comparing the EDS spectra of the Nb and Bi-rich phase of the 1075°C quenched sample and 1150°C 10 hrs. sintered sample (Fig. 95) the decrease in the amount of Nb and Bi in that phase is illustrated.
Fig. 93. TEM image and EDS spectra of grains with different compositions in 1150°C 10 hrs. sintered and 0.05 mol doped sample.
Fig. 94. TEM BF images of grains with different compositions in the 0.05 mol doped and 1150°C 10 hrs. sintered sample.
Fig. 95. EDS spectra of the Nb- and Bi-rich phase in (a) 1100°C air quenched and (b) 1150°C 10 hrs. sintered samples.
CHAPTER V

DISCUSSION

In the previous chapter, sintering, dielectric properties and microstructural characterization results were presented. The characteristic core-shell structure was only observed in Bi$_2$O$_3$ and Nb$_2$O$_5$ doped samples. It was found that this unique structure changes with sintering time and a homogeneous non-ferroelectric phase containing Nb and Bi formed after sintering at 1150°C for 20 hrs. The core-shell structure is the major theme of this study. Sintering, formation mechanism, microstructural characterization and dielectric properties of materials showing this characteristic structure are discussed in this chapter.

A. Sintering

The sintering temperature of BaTiO$_3$ was significantly reduced from 1350°C to 1100-1150°C by the addition of 0.03 mol or 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$), Fig. 26. The shrinkage behavior of the binary doped (Bi and Nb oxides) systems also differed from that of singly doped (Bi$_2$O$_3$ or Nb$_2$O$_5$) BaTiO$_3$. 

181
A. 1. Effects of Nb₂O₅ and Bi₂O₃

Fig. 24 showed that Nb₂O₅ did not change the sintering behavior of BaTiO₃. Dense Nb-doped BaTiO₃ could only be obtained after 1350-1400°C. Previous studies [99-101, 117] have shown the sintering temperature for niobium-doped BaTiO₃ was always above 1400°C.

Bi₂O₃, on the other hand, is a sintering aid which reduces the sintering temperature [118, 120]. Gawrychowska, et al. [113] studied the powder mixture of BaTiO₃ and Bi₂O₃ (ratio 2:3) and found sintering started at 740°C, which corresponded to the melting point of a mixture with BaTiO₃/Bi₂O₃. In this work, shrinkage of 0.1 mol Bi₂O₃-doped BaTiO₃ started at about 720°C. However, it was found that full density could not be obtained in 0.1 mol Bi₂O₃-doped BaTiO₃, Fig. 25. After heating to 1350°C only 10% linear shrinkage was observed.

During heating the powder mixture of BaTiO₃ with 0.1 mol Bi₂O₃ significant weight loss was also observed (Fig. 36). After heating to 1150°C 1.35% weight loss was detected, and more than 16% initial weight was lost at 1400°C. Moreover, the 0.1 mol Bi₂O₃-doped and 1150°C 40 hrs. sintered BaTiO₃ only has a density of 5.224 g/cm³. A microstructure study of this 1150°C 40 hrs. sintered material revealed a dense surface layer and many large interior pores (30-100 μm), as shown in Fig. 33. The pores formed in the
sintered material (Fig. 33) and the low linear shrinkage (Fig. 25) show that Bi$_2$O$_3$ cannot fully densify BaTiO$_3$ during sintering. The resulting low density, large pores and low linear shrinkage are most likely caused by the volatization of Bi$_2$O$_3$.

Bi$_2$O$_3$, from this and other studies [e.g. 116], is known to be a volatile compound (Fig. 34). However, the vapor pressure of Bi$_2$O$_3$ at 1150°C was not reported in available thermodynamic data [126-127]. On the other hand, the reaction free energy of the decomposition of Bi$_2$O$_3$(s) into Bi(g) and O$_2$(g), i.e. Bi$_2$O$_3$(s) $\rightarrow$ 2 Bi(g)+3/2 O$_2$(g), is available [126]. Since sintering was conducted in air, the oxygen pressure is about 0.2 atm. The decomposed Bi(g) vapor pressure at 1400°C is calculated as about 9.1 x 10$^{-6}$ atm, and is about 8.6 x 10$^{-4}$ atm at 1600°C. The decomposed Bi(g) vapor pressure is much less than 1 atm. Therefore, the formation of large pores cannot attributed to the decomposition of Bi$_2$O$_3$, and the sublimation of Bi$_2$O$_3$ at the sintering temperature 1150°C may then play an important role.

Near the surface edge, the volatized Bi$_2$O$_3$ could easily evaporate out. Sintering between the BaTiO$_3$ grains then resulted in a dense surface layer without large pores. On the other hand, in the interior, the volatized Bi$_2$O$_3$ could not diffuse through the dense surface layer, large pores and low density then resulted. Low density in Bi-doped BaTiO$_3$ was also observed by Swilman, et al. [114]. They found with the addition of 2 m/o (Bi$_2$O$_3$+1.5 TiO$_2$) in
the addition of 2 m/o (Bi2O3+1.5 TiO2) in BaTiO3 sintered at 1400°C for 3 hrs., only about 85% density was obtained.

Barium titanate doped with Bi2O3+ Nb2O5 (0.03 or 0.05 mol) showed different sintering behavior than the singly-doped system (Fig. 24-26). With 0.05 mol (Bi2O3+ Nb2O5) the sintering temperature could be reduced to 1100°C and a high density (5.78 g/cm³) was still obtained even after only 1 hr. sintering. Lower binary dopant content (0.03 mol Bi and Nb oxides) material required a slightly higher sintering temperature, but a high density could always be obtained after 1150°C sintering (Fig. 23, 27). The shrinkage curve of 0.1 mol Bi2O3-doped BaTiO3 showed a sharp drop starting at 720°C. After about 5% shrinkage, densification progressed slowly (Fig. 25). In the Nb-doped sample, no shrinkage appeared before 1100°C, Fig. 24 (b). In the Bi and Nb doped BaTiO3, however, rapid densification started at about 1100°C but no shrinkage occurred at 740°C (Tm of 3 Bi2O3.2 BaTiO3) or 825°C (Tm of Bi2O3).

These observations lead to the conclusion that in Bi2O3 and Nb2O5 doped BaTiO3 the rapid densification at 1100°C is not caused by melting of Bi2O3 or (3 Bi2O3.2 BaTiO3). However, the mechanism of the rapid shrinkage behavior of binary-doped BaTiO3 is still not clear. Clearly, the densification mechanism involves a combined effects of both Bi2O3 and Nb2O5. Without the presence of Nb2O5, volatile Bi2O3 cannot sinter BaTiO3 to high density.
In contrast to the 0.03 and 0.05 mol Bi and Nb doped samples, the 0.01 mol Bi and Nb doped samples showed a low density (4.74 g/cm³) after sintering at 1150°C for 1 hr., and the density steadily increased with sintering time. This different sintering behavior of the 0.01 mol Bi and Nb doped samples is possibly caused by the less dopant contents. Owing to the less amount of Bi₂O₃ and Nb₂O₅, densification was not apparent at the beginning of 1150°C sintering.

Bi₂O₃ helped to reduce the sintering temperature of BaTiO₃, but this volatile compound also affected the final density of Bi and Nb doped BaTiO₃. Fig. 27 illustrates that with 0.03 or 0.05 mol (Bi₂O₃+Nb₂O₅) sintered at 1150°C the density steadily decreased with sintering time. In addition, longer sintering times (Fig. 27) and higher sintering temperatures (Fig. 29) resulted in more density decrease in the 0.05 mol binary-doped samples. It is believed that the density decrease is associated with the dopants, Bi₂O₃ and Nb₂O₅. Larger amount of dopants intensifies the dopant effect, and causes more density decrease in higher temperatures and longer sintering times.

In addition to the apparent density decrease in 0.05 mol Bi and Nb doped samples, large pores (30-400 μm) were observed in samples fired for a long time (1150°C for 40 hrs.) or at a high temperature (1250°C for 1 hr.) (see Figures 30-32). TGA analysis, Fig. 37 and 38, revealed that, upon heating, weight loss occurred in 0.05 mol Bi and Nb doped BaTiO₃. EDS analysis, on the other hand,
proved that Bi evaporated out during densification and no Ba, Ti or Nb was detected (Fig. 39). This observation indicated the sublimation of Bi$_2$O$_3$ and/or the evaporation of Bi(g). However, the possible release of oxygen during sintering cannot be excluded.

Drofenik, et al. [105] found that upon sintering BaTiO$_3$ with less than 0.4 mol% Nb, oxygen was released. They noted using TGA that when the Nb content was >0.4 mol% no weight loss was detected. In this study the Nb content (about 8.3 mol% of NbO$_{2.5}$) is much higher than the limit (0.4 mol%) reported by Drofenik, et al. However, the presence of Bi$_2$O$_3$ may affect this upper limit so that the formation of large pores in the sintered material may also involve the release of oxygen. Oxygen can be released in Bi and Nb doped BaTiO$_3$ by following reaction:

$$\text{BaTiO}_3 \rightarrow \text{Bi}_2\text{O}_3 + \text{Nb}_2\text{O}_5$$

$$\text{2 Bi}_\text{Ba} + 2 \text{Nb}_{\text{Ti}} + 4 \text{e}^- + 6 \text{O}_0 + \text{O}_2$$

When the donors, Bi and Nb, substitute for Ba and Ti and the extra charges are compensated by electrons, oxygen gas can be released; but unfortunately, whether oxygen was released or not has not been checked.

As well as density decrease and pore formation, the binary doped samples swelled up during sintering. The diameter of the 1150°C sintered and 0.05 mol binary doped sample increased from 11.954 mm of the 1 hr. sample to 12.466 mm of the 40 hr. sample.
The swelling of the sintered samples indicate the vapor pressure of the volatized gas is very high (possibly larger than 1 atm). Since no detailed analysis was attempted, the exact reason for swelling in sintered samples is still not clear. However, the TGA, shrinkage behavior and microstructure study results suggest that the sublimation of Bi$_2$O$_3$ relates to the observed swelling in sintered samples.

Consequently, the density decrease in Bi and Nb doped samples sintered for long times or high temperatures can be explained by the formation of large pores in the sintered material; and the formation of large pores is possibly caused by sublimation of bismuth oxide and/or the release of oxygen. Due to the dense surface layer, the vaporized and released gas species cannot diffuse out. Therefore, large pores form in the interior and the samples swell. Larger amount of Bi$_2$O$_3$ (0.05 mol) or higher sintering temperature (1250°C) enhance the vaporization of Bi$_2$O$_3$ and oxygen release. A lower density then results (see Fig. 27-29). Indeed, TGA showed that weight loss increased with higher heating temperatures and longer heating times (Fig. 37, 38). Therefore, the sintering treatment of BaTiO$_3$ containing Bi$_2$O$_3$ should be carefully controlled. Kolar and Drofenik made a similar observation in sintered strontium ferrite [116]. When bismuth oxide was added as a sintering aid, high temperatures or longer times did not increase the final density and large pores were observed.
A. 2. Reactions during the sintering process

Both endothermic and exothermic peaks were observed in the DTA curves of binary-doped materials (Fig. 40), but the DTA curves of 0.03 and 0.05 mol Bi and Nb doped samples showed different peaks. Since no BaTiO₃-Bi₂O₃-Nb₂O₅ phase diagram is available, the exact reactions occurred during sintering of the 0.03 and 0.05 mol doped samples are not clear. The peaks in DTA curves, however, indicate reactions occurred during sintering of Bi and Nb doped BaTiO₃.

Powder X-ray diffraction further showed that extra peaks are observed in 0.05 mol (Bi₂O₃+Nb₂O₅) doped and air-quenched samples, Fig. 43-44. It is known that Bi₂O₃ preferably and easily reacts with Nb₂O₅ to form BiNbO₄ (see section IV A. 5.). Nevertheless, the observed extra XRD peaks in air quenched and 0.05 mol binary doped samples are neither from BiNbO₄ nor from the initial dopant oxides, (see Fig. 42-46).

The microstructural study revealed a Nb- and Bi-rich phase in 0.05 mol Bi and Nb doped samples (Fig. 87, 89, 93). EDS analysis showed this Nb- and Bi-rich phase to contain not only Bi and Nb but also Ba and Ti. Even though the composition of the Nb- and Bi-rich phase changed during sintering (Fig 95), this phase still remained after firing at 1150°C for 10 hrs. Similarly, in the 0.05 mol Bi and Nb doped samples the XRD extra peaks were also observed after 1150°C 100 hrs. firing (Fig. 46 (b)). Since no extra TEM electron diffraction spots were observed in the grain shell, no superlattice
structure seems to exist in Bi and Nb-containing BaTiO$_3$ solid solution. In addition, no precipitates were ever observed either on the boundaries or inside the grains. Therefore, the extra peaks in XRD are most likely from the Nb- and Bi-rich phase, and this dopant-rich phase is a reaction product of the dopants and BaTiO$_3$ during sintering. Owing to the lack of BaTiO$_3$-Bi$_2$O$_3$-Nb$_2$O$_5$ phase diagram, this Nb- and Bi-rich phase was not identified. Similarly, the phase diagram of BaTiO$_3$-Bi$_2$O$_3$ is not available either, and the second phase in the 0.1 mol Bi$_2$O$_3$ doped BaTiO$_3$ is not identified.

The formation of a single Nb- and Bi-rich phase instead of forming separate Bi-rich and Nb-rich phases because of segregation during sintering is very interesting. In the 0.1 mol Bi$_2$O$_3$ doped samples, a Bi-rich second phase was observed, as shown in Fig. 6. With the presence of Nb$_2$O$_5$, however, Bi$_2$O$_3$ was always found reacted with Nb$_2$O$_5$. Now, Bi$_2$O$_3$ is a volatile compound with a low melting temperature. Therefore, it is postulated that, during sintering of the Bi$_2$O$_3$ and Nb$_2$O$_5$ doped BaTiO$_3$, Bi$_2$O$_3$ is transported by the vapor or liquid to preferentially react with Nb$_2$O$_5$ and BaTiO$_3$. Consequently, instead of forming separate dopant-rich phases, a Nb plus Bi-rich phase formed.

In addition to the formation of a Nb- and Bi-rich phase during sintering, BaTiO$_3$ grains also show compositional and structural changes in samples sintered with 0.03 or 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$). EDS analysis, clearly illustrated that after sintering at 1150°C for 20 hrs. all the BaTiO$_3$ grains changed into a
non-ferroelectric solid solution containing Bi and Nb. In addition, XRD revealed that after sintering at 1150°C for 100 hrs. both the 0.03 and 0.05 mol doped sample were cubic at room temperature (Fig. 47), and the lattice parameter increased with the dopant content. After sintering at 1150°C for 100 hrs. the lattice parameters of BaTiO₃ in the 0.03 and 0.05 mol doped samples were 4.0146 and 4.0160 respectively, and the deviation was 0.1%.

Subbarao [99] showed that with 3 to 4 mol% of NbO₂ added, sintered BaTiO₃ had a cubic structure at room temperature. Baxter[115] studied 5 mol% Bi₂O₃ doped and 1350-1420°C sintered BaTiO₃, and found the sintered material remained tetragonal at room temperature. In this work, a cubic structure is observed in the BaTiO₃ solid solution containing Bi and Nb. Consequently, it seems Nb is more effective in modifying the BaTiO₃ crystal structure and transforming the ferroelectric tetragonal structure into a non-ferroelectric cubic one at low temperature.

Microstructural and EDS chemical analysis revealed that a BaTiO₃ solid solution containing Nb and Bi is thermodynamically favored in the system of BaTiO₃ with 0.05 mol or 0.03 mol (Bi₂O₃+Nb₂O₅). This conclusion was clearly illustrated by the evolution of the microstructure (Fig. 57-58) and the dopant concentration profiles in grains sintered for 0.5, 4 and 10 hrs. (Fig. 77 and 85). EDS concentration profiles, Fig. 77 and 85, further show that the Bi and Nb profiles are parallel to each other.
Unfortunately, quantification of the mole ratios of Bi, Nb, Ba and Ti in the solid solution was not successful. These concentration profiles, however, still qualitatively reveal the co-solubility of both of the dopants in BaTiO$_3$ at a low temperature (1150°C). In addition, Bi and Nb are believed to replace Ba and Ti respectively. If both Bi and Nb ions substitute for either Ba or Ti ion, a Ba- or Ti-rich phase should occur. However, no Ba- or Ti-rich phase was observed, and no precipitates or 2nd phase was detected in the BaTiO$_3$ solid solution grains or on their boundaries.

B. Core-Shell Structure

In this study, the core-shell structure was only observed in samples doped with Nb$_2$O$_5$ and Bi$_2$O$_3$. In 0.1 mol Bi$_2$O$_3$ doped BaTiO$_3$, the core-shell structure was never observed, but a Bi-rich second phase was found along the boundaries. Generally, the core-shell structure changed with sintering time (Fig. 57-58) and the ferroelectric grain core was eliminated after sintering at 1150°C for 20 hrs. In this section, the discussion is focused on the microstructure evolution and the characteristics of the cores and the shells.

B. 1. Ferroelectric grain cores and non-ferroelectric grain shells

The characteristic feature of the core-shell structure is that ferroelectric domain fringes only appeared in the grain cores
for 20 hrs. In this section, the discussion is focused on the microstructure evolution and the characteristics of the cores and the shells.

B. 1. Ferroelectric grain cores and non-ferroelectric grain shells

The characteristic feature of the core-shell structure is that ferroelectric domain fringes only appeared in the grain cores but not in the shells. Despite the apparent image difference, the major difference between the core and the shell is composition. Fig. 73 clearly showed that the grain shell was a BaTiO3 solid solution containing Bi and Nb. The grain core, on the other hand, was relatively pure BaTiO3. In fact, EDS results (Fig. 74-76) revealed that the non-ferroelectric shell was actually formed by the incorporation of Bi and Nb into the BaTiO3 lattice. Associated with the existence of dopants in the shell is the disappearance of the ferroelectric domains. The appearance of the core-shell structure and the evolution of this unique structure is related to the distribution of the dopants (in this case Bi and Nb) in the sintered BaTiO3.

The existence of ferroelectric domains (at room temperature) in the grain core was confirmed by comparing the images at temperatures above and below Tc (Fig. 66) and by the splitting of the electron diffraction spots from the grain core in the TEM
observations evidently show that ferroelectric domains still exist in small grains (<1 um).

The observation of domain boundaries in small grains (<1 um) is apparently contradictory to Buessem's assumption [34, 35] and Yamaji's result [65, 66], but is consistent with the observation by Arlt [31]. Arlt showed that the domain boundaries were not easily revealed on the surface by chemical etching, especially in small grains with small distances between the domain boundaries. Therefore, the discrepancy is caused by the analysis methods and it is believed that results confirmed by TEM image contrast and electron diffraction patterns are more reliable. Other TEM studies of the temperature-stable dielectrics also show ferroelectric cores with typical domain fringes in grains less than 1 um size [118-121].

TEM microstructural investigation (Fig. 64-66) showed that there are no distinct phase boundaries between the grain cores and the grain shells, and the electron diffraction patterns (Fig. 67) demonstrate the structural continuity between them. EDS chemical analysis (Fig. 74-76) further revealed that the dopant concentration decreased gradually from the shell to the core center with no sharp compositional difference at the core-shell boundaries. These observations indicate that the grain core and the grain shell are completely coherent, and the reason for this characteristic core-shell image in TEM is associated with the content of the dopants. In
addition, the coherence between the ferroelectric grain core and the non-ferroelectric grain shell could be explained by the broad diffuse-interface model, proposed by Malis and Gleiter [63].

From the Bi and Nb concentration profiles (Fig. 77), the count ratios of Bi/Ba+Ti and Nb/Ba+Ti at the core-shell boundaries are about 0.043-0.047 and 0.02-0.025 respectively. Statistical variations of the counts in EDS spectrum peaks definitely exist and are within the range of 10%. These observations still suggest that there must exist certain Bi and Nb concentration limits, above which the material is no longer ferroelectric. When the Bi and Nb contents exceed the concentration limits, the lattice transforms into cubic and is non-ferroelectric. On the other hand, when the concentrations are below the limits, the tetragonal ferroelectric state remains. Although it was not possible to correlate quantitatively the count ratios with actual concentrations, at -174°C, the critical ratios of Bi/Ba+Ti and Nb/Ba+Ti are in the ranges of 0.043-0.047 and 0.02-0.025 respectively. Similarly, Subbarao [99] observed that there existed a Nb concentration limit, above which the original tetragonal BaTiO₃ lattice changed to cubic. In his work he found the Nb concentration limit at room temperature was 3 to 4 mol% which is not too different from that found here.

EDS chemical analysis showed that at a fixed temperature the nature of the BaTiO₃ lattice, ferroelectric or non-ferroelectric, was determined by the dopant concentrations. Both the Bi and Nb
concentrations gradually decrease from the shell toward the core center. On the other hand, Fig. 78 and 79 illustrate that the size of the ferroelectric grain cores gradually diminishes by raising the specimen temperature from -174°C to 140°C. The size reduction in the ferroelectric grain cores indicates that associated with the gradual decrease of dopant content in the core the ferroelectric to non-ferroelectric transformation temperature is increased. At 140°C, above the Tc of BaTiO₃, the whole grain is non-ferroelectric. Furthermore, as shown in Fig. 74-76 and 78-79, at -174°C, a large area surrounding the ferroelectric core remains non-ferroelectric.

These observations show the importance of the dopant concentrations in determining the lattice structure and the transformation temperature. Higher dopant (Bi and Nb) contents in BaTiO₃ decrease the ferroelectric to non-ferroelectric transformation temperature, Tc. The observed core-shell structure simply reflects the effect of the dopants in modifying the structure, and the evolution of the core-shell structure was mainly a result of the dopant distribution during sintering. When the dopant is homogeneously distributed and the dopant contents are above the limit for transformation, no core-shell structure is seen. The mechanisms which determine the transport and distribution of the dopants are, consequently, critical to understanding the development of this microstructure.
B. 2. The core-shell structure formation mechanism

Hennings, et al. [119] proposed a solution-precipitation model to explain the formation of the core-shell structure which was observed in the 1200°C sintered BaTiO₃ with 0.03 mol "CdBi₂Nb₂O₉" as additives. However, the authors did not confirm the presence of a liquid phase by any microstructural study. The proposition was mainly based on the observation of some endothermic and exothermic peaks in DTA. The authors attributed these DTA peaks to the formation of a melt containing the additives. In contrast to Henning's proposal, Rawal, et al. [118] suggested that the dopants, Bi and donors such as Nb or La, were distributed by fast grain boundary diffusion, and dopants were incorporated into the perovskite grain by grain growth. Again no clear microstructural results were presented by Rawal. The only careful microstructural investigation about the core-shell structure was provided by Mecartney, et al. [121]. In their study, high resolution lattice imaging confirmed that no second phase existed at grain boundaries down to a width of 1-2 nm, and no precipitates were observed.

In the present work, the grain boundary regions were carefully examined. No amorphous or other second phase were ever observed. Instead, clear boundary fringes, boundary ledges (Fig. 82) and many dislocations (Fig. 80, 81) occurred on the grain boundaries. EDS point analyses showed no evidence for the existence of a dopant-rich phase on the boundaries. Consequently, the
existence of a liquid phase which promotes the core-shell structure is unlikely. As a result, the distribution or transport of the dopants is most likely by solid diffusion. Since the core-shell structure was observed throughout the sintered material and in grains of different sizes, rapid grain boundary diffusion must be responsible for the dopant distribution. Furthermore, if a liquid phase was present at the sintering temperature which then froze epitaxially on existing grains, an abrupt change in dopant concentration with distance would be expected. All concentration profiles showed only a gradual change in composition suggesting a diffusion process rather than liquid solidification.

The transport of dopants through grain boundary diffusion is supported by the EDS point analysis results. Fig. 77 and 85 show the Bi and Nb concentration profiles across the grains and boundaries of samples treated at 1150°C for different times. All the profiles show that the dopant concentrations gradually decrease toward the core centers. The concentration change are gradual and no abrupt compositional changes were observed. At the early stage of sintering (fired for 0.5 hr.), the boundary region was enriched with dopants and the dopant content in the core was very small. This profile further indicates the grain boundary diffusivity is high. With longer sintering, the dopants diffuse from the boundaries into the grains. Ten hours sintering at 1150°C makes the dopant distribution more homogeneous and the core shows higher dopant contents. On the other hand, during this homogenization process, no boundary phase
was observed but dislocations and ledges. Consequently, it is believed that the distribution of dopants during sintering proceeds by a diffusion mechanism. By a combination of grain boundary and lattice diffusion the dopants are gradually homogeneously distributed and the total amount of dopants inside a grain increases, see Fig. 77 and 85.

A Nb- and Bi-rich phase was observed in 1075 and 1100°C air quenched samples (Fig. 87, 91). This dopant-rich phase showed a crystalline structure and did not penetrate through the boundaries between BaTiO₃ grains, as shown in Fig. 89 and 94, suggesting that at no time was it liquid. EDS analysis revealed the existence of Bi and Nb in grains neighbouring this dopant-rich phase (Fig. 88 and 91). In grains farther away, no dopants were detected. By comparing the EDS spectra of the Bi- and Nb-rich phase in the 1100°C air quenched sample with that of the 1150°C 10 hrs. fired sample (Fig. 95), the decrease in the amount of Nb and Bi in that phase was evidently illustrated. This suggests that during sintering of Bi₂O₃ and Nb₂O₅ doped BaTiO₃, this Bi- and Nb-rich phase acts as a source of the dopants.

From the observations discussed above, the formation of the core-shell structure can be assumed to proceed in the following steps, as illustrated in Fig. 96. At the beginning of sintering, Bi₂O₃ and Nb₂O₅ react with BaTiO₃ and form the unidentified Nb- and Bi-rich phase. Due to the inhomogeneous distribution of Bi₂O₃ and
particles, this dopant-rich phase forms locally in certain regions. This dopant-rich phase acts as a source of dopants and supplies Bi and Nb during sintering. Rapid grain boundary diffusion distributes the dopants throughout the sample leading to higher amounts of dopants near the boundaries. The dopants then diffuse into the BaTiO$_3$ grains by lattice diffusion and a core-shell structure is formed when the outer region of the grain, i.e. the grain shell, has incorporated enough dopants to render it non-ferroelectric.

The diffusion model is not only supported by the observed dopant concentration profiles but also by the microstructural observations. The core-shell structure in small grains would not be expected in the solution-precipitation model [119]. In that model, the smaller grains should dissolve and then precipitate on the large ones. Therefore, in that model the core-shell structure should be observed primarily in large grains. Consequently, the observation of a core-shell structure in all grains supports the diffusion model. Furthermore, the neighbouring grains of the Nb- and Bi-rich phase which transformed into the nonferroelectric solid solution earlier than the other grains also cannot be explained by the solution-precipitation model. The most important observation supporting the diffusion model is that no amorphous or second phases were ever observed at grain boundaries in either slow-cooled or air-quenched samples. Furthermore, the gradual change in dopant concentrations into the grain would be expected only from a diffusion process.
Transportation paths of Bi and Nb.

Fig. 96. Proposed mechanism for the transport of dopants and microstructure evolution.
B. 3. Microstructure evolution and grain growth

$\text{Nb}_2\text{O}_5$ (>0.4 mol%) has been reported as a powerful grain growth inhibitor for $\text{BaTiO}_3$ [101-104]. Similarly, in 5 mol% $\text{Bi}_2\text{O}_3$ doped $\text{BaTiO}_3$, grain growth was also found to be limited [115]. In this study it has been found that in 0.1 mol $\text{Bi}_2\text{O}_3$ doped $\text{BaTiO}_3$, grain growth was completely inhibited even after sintering at $1150^\circ\text{C}$ for 40 hrs., as shown in Fig. 59. The average grain sizes of 1 hr. and 40 hrs. sintered samples are 0.39 and 0.41 um respectively. The reason for the inhibited grain growth in 0.1 mol $\text{Bi}_2\text{O}_3$ doped sample is not clear but it may be associated with the Bi-rich second phase on the grain boundaries. Little Bi was detected in the grains of the sample sintered 40 hrs., and the existence of Bi in $\text{BaTiO}_3$ grains did not effect the ferroelectric nature. The important observation in $\text{Bi}_2\text{O}_3$ doped samples was that no core-shell structure was formed.

The microstructure of Bi and Nb doped samples was very different. The core-shell structure was formed in samples sintered at 1100 and $1150^\circ\text{C}$ for short times (<20 hrs.). In addition, grain growth was observed during sintering, Fig. 48. After firing at $1150^\circ\text{C}$ for 20 hrs. the characteristic core-shell structure was eliminated, Fig. 58. At the same time the average grain size increased to 2.19 um. During the early stages of sintering, due to rapid grain boundary diffusion, the dopant concentrations were enriched on the boundaries of the $\text{BaTiO}_3$ grains. Lattice diffusion
of the dopants then led to the formation of the core-shell structure in both large and small grains. However, simultaneously, grain growth occurred and small grains were eliminated.

Kahn and co-workers [100-101] found that Nb has a fast grain boundary diffusivity and low bulk diffusivity in BaTiO₃, but no grain boundary or bulk diffusion coefficients of Nb in BaTiO₃ were reported. They also showed that the homogeneous distribution of Nb in sintered BaTiO₃ ceramics only existed when significant grain growth occurred. In fact, grain growth is an important step for dopant incorporation into the BaTiO₃ lattice during sintering [118-119].

Upon sintering of BaTiO₃ with Bi and Nb oxides, grain growth was observed. However, the growth was very small. For example, for samples containing 0.05 mol (Bi₂O₃+Nb₂O₅) and sintered at 1150°C, the average grain size increased from 0.57 μm of 0.5 hr. sample to 3.89 μm of 40 hrs. fired sample, as shown in Table III. The estimated grain growth rate is only 0.083 μm/hr. For samples with 0.03 mol dopants or heated at 1100°C the grain growth rates are also small, about 0.08 μm/hr. Even though the growth rate was small, the effect of grain growth on the distribution of the dopants is still significant.

The average core and grain sizes of grains showing a clear core-shell structure were measured and summarized in Tables II and
IV. In addition, the volume fraction of grain cores was calculated. The volume fraction of grain cores significantly decreased with sintering time and sintering temperature. The measured data, on the other hand, shows that for all samples, the size of grains showing a clear core-shell structure is larger than the average grain size of all the observed grains. This discrepancy may be due to the core-shell structure not being detected in very small grains. Therefore, the average grain size of grains with a core-shell structure is larger. Several explanations can be offered to explain why some small grains did not clearly show the core-shell structure. The small grains visible in the image could have been a corner of a large grain, where the BaTiO₃ had already transformed into the non-ferroelectric state. Since the TEM foil specimen cut across that nonferroelectric corner, a small grain without a ferroelectric core would then be detected. Another explanation could be attributed to the diffusion of the dopants. Since the diffusion distance in a small grain is short, it can transform to the non-ferroelectric state more quickly. Consequently, the measured average grain size of the grains showing a clear core-shell structure was larger than the average grain size of all the grains.

Another interesting observation is that the size of the grain core did not decrease with the sintering time for time less than 10 hrs. During sintering, while the average grain size is increasing and the volume fraction of the grain core is decreasing,
the average size of the grain core also shows a very limited increase at the early stages of sintering. For example, in the 0.05 mol doped sample the average core size changed from 0.51 um in the 0.5 hr. sintered sample to 0.56 um in the 4 hr. sample. In the 10 hrs. sintered sample, only three ferroelectric grain cores were observed, and the average size was 0.5 um. After 20 hrs. sintering, all the cores were eliminated.

It could be argued that the observed change in the core size is within the standard deviation of the measurement. Indeed, the standard deviation of the core size measurement was about 0.08 to 0.1 um. However, samples doped with different dopant contents, or heat treated at different temperatures, showed the same trend. For the 0.03 mol doped and 1100°C sintered samples, the core size increased from 0.38 um (0.5 hr.) to 0.47 um (2 hrs.). For the 0.05 mol doped and 1150°C sintered sample, the size increased from 0.51 um to 0.56 um (40hrs.). Consequently, the apparent size change of the grain core cannot be totally attributed to the measurement deviation.

The increase of core size may be attributed to grain growth during sintering. During the early stages of sintering, the core-shell structure forms in all grains. At a later stage of sintering, grain growth occurs and small grains are eliminated. As a result, the number of grains is reduced and the average grain size is increased. Simultaneously, lattice diffusion of the dopants is also
occurring and the dopants are transported into the grains. Due to the combined effect of lattice diffusion and grain growth, only large grains remain and show a clear core-shell structure. The small grains, on the other hand, are either eliminated by grain growth or transformed into nonferroelectric state by diffusion. Consequently, the number of grains which showed a clear core-shell structure was reduced. Since the average core size is measured only in those large grains, and no core-shell structure exists in small grains, the average size of the grain core is then increased. A schematic representation of grain growth and the small grain elimination is illustrated in Fig. 97.

The occurrence of grain growth by solid state diffusion but not through the solution-precipitation process is supported by the microstructural and microchemical data. In the TEM images, the grain cores were generally not at the center of the grains. In addition the dopant concentration profiles, either inside a grain or across a grain boundary, were usually asymmetrical. If the solution-precipitation mechanism was responsible for the formation of a core-shell structure, a uniform layer surrounding the grain core and symmetrical concentration profiles across the grains and the grain boundaries would be expected. However, the observed asymmetrical profiles and the off-centered grain cores further support the hypothesis that the formation of the core-shell structure is determined by diffusion and grain growth without the presence of a
liquid phase. The asymmetrical profile across a grain boundary strongly suggests the influence of the grain boundary migration.

In samples sintered at 1150°C for short times, Fig. 64-66 and 69-72, stacking faults were observed in the grain shell. In samples sintered for longer times, 20 and 40 hrs. no stacking faults were observed. The possible displacement vector of the observed stacking faults is 1/3 <111> or 1/6<112>, and the stacking faults lie on (111) planes. The occurrence of stacking faults in the grain shells may relate to the diffusion of the dopants from the boundaries to the grain cores. However, the exact reason for the formation and the disappearance of these stacking faults is not known.
Fig. 97. A schematic representation of grain growth and the elimination of small grains.
C. Dielectric Properties

The dielectric properties of sintered BaTiO$_3$ are determined by the microstructure and the distribution of the dopants. The intrinsic dielectric properties of BaTiO$_3$ are usually modified by dopants. The microstructure, which includes the porosity and the grain size, also affect the final properties. With the addition of Bi$_2$O$_3$ and Nb$_2$O$_5$, the dielectric properties of doped BaTiO$_3$ changes with heat treatment and the dopant content. The correlation between the microstructure and the dielectric properties will now be discussed.

C. 1. Effects of dopants and sintering treatments

For samples doped with 0.03 or 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$), sintering time had the same effect. Longer sintering times deteriorated the dielectric temperature-stability and increased the variation of dielectric constant, k', over the test temperatures (-55 to 125°C), as illustrated in Figs. 48-50 and 52. Temperature shows a similar effect as sintering time. Higher sintering temperature decreased the temperature-stability of the dielectric constant and increased the variation of k', i.e. $k'/k'(25°C)$. The dopant content had less influence on the dielectric properties. Since the samples tested were all binary doped (Bi and Nb oxides) materials, no evident difference in the dielectric temperature
curves was observed between the 0.03 and 0.05 doped samples. The only difference was that the 0.03 mol doped samples showed higher dielectric constants, Fig. 52 and 53.

The general temperature characteristics of samples treated at different times or temperatures can be understood from the microstructure observations. Samples fired for short times (< 1 hr.) or at a lower temperature (1100°C), formed the characteristic core-shell structure. In addition, the grain-core volume fractions of these samples were still large. For example, the volume fraction of the grain cores in the 1150°C 1 hr. sample was 37.1%. As a result, the dielectric-temperature curves contain contributions from the dopant-containing region and the relatively pure grain core, which results in a temperature-stable dielectric material. In fact, in samples fired at 1100°C and the sample fired at 1150°C for 0.5 hr. an increase of $k'$ at 125°C is clearly illustrated in Fig. 48 and 49. This increase of $k'$ at 125°C is from the pure BaTiO$_3$ region, i.e. the grain core, which raises $k'$ at 125°C. For samples fired at high temperature (1200°C) or longer time (>10 hrs.), the volume fraction of the grain core becomes very small, and the dielectric behavior is mainly determined by the solid solution shell. Since the unidentified Nb-and Bi-rich phase is present only as a minor phase, its dielectric properties can be ignored.
In samples containing 0.05 mol Bi and Nb and sintered for more than 10 hrs., the microstructure showed a homogeneous solid solution with Bi and Nb uniformly distributed. The dielectric measurements show that this solid solution has a continuous decrease of dielectric constant with temperature. The dielectric constants of samples sintered for 10 hrs. or more showed almost the same behavior. Even though $k'$ decreased with sintering time, but the $k'/k'(25^\circ C)$ curves are identical (see Fig. 50). The decrease of $k'$ with longer time is believed to be a result of the density decrease. Furthermore, the solid solution did not show any ferroelectric transformation down to -174°C, as shown in Fig. 78, 79.

Previous studies showed that in BaTiO$_3$ containing 0.03 mol "CdBi$_2$Nb$_2$O$_9"$, the Curie temperature of the dopant-containing region was about -80°C. [119]. When BaTiO$_3$ sintered with 10-12 wt% Bi$_4$Ti$_3$O$_{12}$ and 3 wt% donors (Nb or La), a peak at 25°C was observed [118]. In contrast, this work shows that when the count ratios of Bi/Ba+Ti and Nb/Ba+Ti are over 0.045 and 0.022 respectively no ferroelectric transition occurs over the temperature range -174 to 140°C. In the 10 hrs. fired sample, as shown in Fig. 76, almost the entire grain has a composition over that limit. Consequently, in the samples fired for 10 hrs or more, no dielectric constant peak was observed between -55 to 140°C, Fig. 50.
Another important microstructural observation is that when the dopant concentration becomes lower, a ferroelectric transformation starts to appear at higher temperatures. At the core center, where the dopant content is very low, the transformation temperature is near the Curie temperature of pure BaTiO$_3$ (130°C). Thus, the results indicate that the dielectric properties of a material with a core-shell structure are actually composed of contributions from three distinct regions. One is the solid solution region where no ferroelectric transformation occurs even at -174°C. The second is the relatively pure BaTiO$_3$ core region. The third region is a transition zone, where the dopant content shows a continuous change and the transformation temperature also shows a continuous change from -174 to 130°C (Tc of pure BaTiO$_3$).

The effects of sintering temperature and time on dielectric properties can then be rationalized by their effect on the distribution of dopants. When the sintering temperature is low and the time is short, a chemically inhomogeneous system results. Consequently, the overall dielectric behavior depends on that all three different regions with different temperature characteristics. A temperature-stable dielectric constant curve is then obtained. When the sintering temperature is high or the time is long, a homogeneous material results and the dielectric properties are dominated by the properties of the BaTiO$_3$ solid solution alone.
C. 2. Temperature-stable dielectrics

EIA has specified the X7R materials should have a dielectric constant which does not change by more than 15% from the 25°C reading over the temperature range from -55 to 125°C. According to that specification, the samples containing 0.05 mol Bi and Nb oxides fired at 1100 or 1150°C for less than 2 hrs. and samples containing 0.03 mol dopants sintered at 1150°C less than for 1 hr. belong to this category. All these samples show a core-shell structure. Among them, the 0.05 mol doped and 1100°C 0.5 hr. sintered sample shows the best temperature-stability and the variation of k' is less than 3%.

A detailed model of the effect of the observed microstructure on the temperature dependence of the dielectric constant is probably not realistically possible. However, an approximate model can be attempted by applying the logarithmic mixing rule [124] to the three different regions: the core, the shell, and the transition region. To determine the effects of the transition region, its behavior is first ignored. Ignoring the effect of the transition zone and simply applying the logarithmic rule to the mixture of the core and a solid solution shell:

\[
\log k_m' = V_s \log k_s' + V_c \log k_c' \tag{7}
\]

where \( k' \) is the dielectric constant, \( V \) the volume fraction and the subscripts \( m, s, \) and \( c \) indicate the mixture, shell and core. In this
calculation the dielectric constants of 0.05 mol doped samples which have a core-shell structure are used to represent the dielectric constants of the core-shell mixture. In addition, the volume fraction of the core and shell are measured and listed in Tables II and IV. Since we know the 1150°C 10 hrs. fired sample shows complete solid solution behavior, the dielectric constants of that sample are used for $k_s'$ values. Thus, the dielectric constants of the grain core at different temperatures can be calculated by applying the logarithmic equation (7).

The calculated dielectric constants of the grain cores in three different samples are plotted in Fig. 98. The dielectric constant of pure BaTiO$_3$ [125] is also plotted for comparison, as shown in Fig. 98. Evidently the grain cores do not behave like pure BaTiO$_3$, and the most apparent deviation is that the grain core of the measured samples do not show a sharp dielectric constant peak at 125°C. Consequently, assuming the grain core is pure BaTiO$_3$ is not appropriate.

Another way to evaluate the two-phase mixing model is to assume the core is pure BaTiO$_3$ and compare the dielectric constants of a solid solution (1150°C 10 hrs. sintered sample) to the calculated $k_s'$ of the grain shells. The calculated results (solid lines) and the $k'$ of 1150°C 10 hrs. sintered sample (dashed line) are shown in Fig. 99. Obviously, the calculated data also do not match the real behavior of a solid solution, especially at the high
temperature end (125°C). As a result, to express the real dielectric behavior of a temperature-stable material, the contribution from the transition zone cannot be ignored. The dielectric constant of a material showing the core-shell structure should then be expressed by:

$$\log k_m' = V_s \log k_s' + V_c \log k_c' + V_t \log k_t'$$  (8)

where $V_t$, and $k_t'$ represent the volume fraction and dielectric constant of the transition zone. Since the exact volume fraction of the transition zone was not accurately measured, the volume fraction of these three different regions are roughly estimated from the EDS concentration profiles, Fig 74. For the 0.5 hr. sintered sample at -174°C, the volume fraction of the solid solution shell is 60%, the relatively pure BaTiO₃ is 4% and the transition zone is 36%. By using the dielectric constants of 0.5 hr. fired sample as $k_m'$, the $k'$ of 10 hrs. sintered sample as $k_s'$ and the value of pure BaTiO₃ as $k_c'$, the values of $k_t'$ at different temperatures can then be calculated. The calculated results are plotted in Fig. 100. As shown in Fig. 100, the $k_t'$ vs temperature curve is very stable with a slight increase toward 125°C. The average value of the calculated $k_t'$ is around 1400. A relatively flat dielectric constant with temperature of the transition zone is expected because the transition zone is composed of regions which undergo the non-ferroelectric to ferroelectric transformation at different temperatures, continuously from -174 to 130°C. A schematic figure
showing the dielectric behaviors of the core, the shell and the transition zone is illustrated in Fig. 101.

Since the dielectric constant of the transition zone is flat, this suggests how to optimize such inhomogeneous dielectrics. Obviously, if the dopant concentration, firing time and temperature can be controlled such that the transition zone fills the whole grain, this will be the optimum microstructure.
Dielectric Constant of Core

If shell is Solid Solution 1150°C 10 hrs.

Fig. 98. Dielectric constant of the grain core (by using two-phase mixture model).
Dielectric Constant of Shell

Relative Dielectric Constant, $k'$

If core is pure BeT103

Fig. 99. Dielectric constant of grain shell (assume two-phase mixture model).
Dielectric Constant of Transition Zone

Relative dielectric constant, $k'$

Assume solid solution 1150 10hrs.
Assume core pure BaTiO$_3$

Fig. 100. Dielectric behavior of transition zone.
Fig. 101. A schematic representation of the dielectric behaviors of the shell, the core and the transition zone.
(1) The core-shell structure formed in 0.05 mol and 0.03 mol (Bi$_2$O$_3$ +Nb$_2$O$_5$) doped BaTiO$_3$, but not in 0.1 mol Bi$_2$O$_3$ doped samples.

(2) The grain shell was a non-ferroelectric BaTiO$_3$ solid solution containing Bi and Nb with a cubic structure.

(3) The ferroelectric grain core was relatively pure BaTiO$_3$ with a tetragonal crystal structure.

(4) The presence of ferroelectric domains in grain cores was confirmed by electron diffraction pattern analysis and by comparing the TEM images above and below Tc.

(5) The concentration and distribution of the dopants determined the evolution and morphology of the core-shell structure.

(6) The formation of the core-shell structure was facilitated by rapid grain boundary diffusion of dopants followed by lattice diffusion. The dopants were supplied by a Nb- and Bi-rich phase.

(7) Diffusion and grain growth influence the transport and the distribution of the dopants.
(8) No second phases or precipitates were observed on grain boundaries or in the shell, but stacking faults were observed in the grain shell. There was no evidence for the presence of a liquid phase during sintering.

(9) The core-shell interface was completely coherent. No boundary fringes were observed at the core-shell interface. Dislocations and boundary ledges, however, occurred on the grain boundaries.

(10) The sintering temperature was reduced to 1100-1150°C by the addition of 0.03 or 0.05 mol (Bi$_2$O$_3$+Nb$_2$O$_5$), but the density decreased with sintering time and temperature.

(11) Bi$_2$O$_3$ was a volatile compound. Weight loss, pore formation, low shrinkage and density decrease were all related to the volatilization of Bi$_2$O$_3$ during sintering.

(12) The dielectric temperature-stability of material with the core-shell structure contains contributions from three distinct regions, i.e. the solid solution shell, pure BaTiO$_3$ core, and the transition zone.

(13) The BaTiO$_3$ solid solution containing Nb and Bi had a cubic structure and did not transform to the ferroelectric state at temperatures down to -174°C. The dielectric constant of the solid solution decreased with temperature.
The transition zone is a region with continuous changing composition and underwent non-ferroelectric to ferroelectric transformation continuously from -174°C to 130°C. The temperature characteristic of this transition zone is a flat dielectric constant curve.
APPENDIX A

Density and Diameter of BaTiO₃ with 0.05 mol. (Bi₂O₃ + Nb₂O₅)

A. Sintered at 1150°C

<table>
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B. Sintered at 1100°C

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C. Sintered for 1 hour

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223
APPENDIX B

Density and Diameter of BaTiO₃ with 0.03 mol. (Bi₂O₃ + Nb₂O₅)

A. Sintered at 1150°C

<table>
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B. Sintered for 1 hour

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APPENDIX C

Density and Diameter of BaTiO$_3$ with 0.01 mol. (Bi$_2$O$_3$ + Nb$_2$O$_5$)

A. Sintered at 1150°C

<table>
<thead>
<tr>
<th>Time (hr.)</th>
<th>Density (g/cm$^3$)</th>
<th>Diameter (mm)</th>
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<td>100</td>
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<td>11.883</td>
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A. BaTiO$_3$ + 10 mol\% (Bi$_2$O$_3$, Nb$_2$O$_5$)
APPENDIX E

Dielectric Data for BaTiO$_3$ with 0.05 mol. (Bi$_2$O$_3$ + Nb$_2$O$_5$)

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<th>65</th>
<th>85</th>
<th>105</th>
<th>125</th>
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<td>955</td>
<td>932</td>
<td>908</td>
<td>887</td>
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<td>-5.0</td>
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<td>0.014</td>
<td>0.006</td>
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<td>0.002</td>
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<td>0.001</td>
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### B. Sintered at 1100°C

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<th>25</th>
<th>45</th>
<th>65</th>
<th>85</th>
<th>105</th>
<th>125</th>
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</thead>
<tbody>
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### C. Sintered for 1 hr.

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<td>837</td>
<td>855</td>
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<td>Δk'/k'(%)</td>
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<td>2.6</td>
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<td>0.008</td>
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<td>14.3</td>
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<td>-14.5</td>
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### APPENDIX F

Dielectric Data for BaTiO$_3$ with 0.03 mol. (Bi$_2$O$_3$ + Nb$_2$O$_5$)

**Sintered at 1150°C**

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<th>Sintering time (hr.)</th>
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<td></td>
<td></td>
<td>$k'$</td>
<td>$\Delta k'/k'(%)$</td>
<td>$\tan \delta$</td>
<td>$k'$</td>
<td>$\Delta k'/k'(%)$</td>
<td>$\tan \delta$</td>
<td>$k'$</td>
<td>$\Delta k'/k'(%)$</td>
</tr>
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APPENDIX G

A. Count, Mean and Standard Deviation of Measured Grain Size of Bi$_2$O$_3$ and Nb$_2$O$_5$ Doped BaTiO$_3$ Sintered at 1100°C

<table>
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<th>1 hr.</th>
<th>2 hrs.</th>
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<td>0.45 um</td>
<td>0.55 um</td>
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<td>s. dev.</td>
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<td>0.25 um</td>
<td>0.27 um</td>
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<td>120</td>
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<tr>
<td>0.05 mol</td>
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<tr>
<td>mean</td>
<td>0.51 um</td>
<td>0.52 um</td>
<td>x</td>
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<tr>
<td>s. dev.</td>
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</table>
B. Count, Mean and Standard Deviation of Measured Core and Grain Sizes of Grains with Core-Shell Structure in Bi$_2$O$_3$ and Nb$_2$O$_5$ doped BaTiO$_3$ sintered at 1100°C

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<tr>
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<th>1 hr.</th>
<th>2 hrs.</th>
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<tr>
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<tr>
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<td>0.67 μm</td>
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<td>0.26 μm</td>
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<td>0.18 μm</td>
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<td>52</td>
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<tr>
<td>Mean</td>
<td>0.48 μm</td>
<td>0.50 μm</td>
<td></td>
</tr>
<tr>
<td>S. Dev.</td>
<td>0.25 μm</td>
<td>0.25 μm</td>
<td></td>
</tr>
<tr>
<td>Count</td>
<td>27</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Core Vol. %</td>
<td>44.2</td>
<td>34.9</td>
<td></td>
</tr>
</tbody>
</table>


APPENDIX H

A. Count, Mean and Standard Deviation of Measured Grain Size of 0.05 mol (Bi₂O₃+Nb₂O₅) doped BaTiO₃ Sintered at 1150°C

<table>
<thead>
<tr>
<th>sintering time</th>
<th>0.5 hr.</th>
<th>2 hrs.</th>
<th>4 hrs.</th>
<th>10 hrs.</th>
<th>20 hrs.</th>
<th>40 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>grain size</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>0.57um</td>
<td>0.91um</td>
<td>1.39um</td>
<td>1.55um</td>
<td>2.19um</td>
<td>3.89um</td>
</tr>
<tr>
<td>s. dev.</td>
<td>0.30um</td>
<td>0.33um</td>
<td>0.54um</td>
<td>0.59um</td>
<td>0.99um</td>
<td>1.77um</td>
</tr>
<tr>
<td>count</td>
<td>20</td>
<td>18</td>
<td>48</td>
<td>32</td>
<td>24</td>
<td>10</td>
</tr>
</tbody>
</table>

B. Count, Mean and Standard Deviation of Measured Core and Grain Sizes of Grains with Core-Shell Structure in 0.05 mol (Bi₂O₃+Nb₂O₅) doped BaTiO₃ sintered at 1150°C

<table>
<thead>
<tr>
<th>sintering time</th>
<th>0.5 hr.</th>
<th>2 hr.</th>
<th>4 hr.</th>
<th>10 hrs.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>grain size</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>0.71 um</td>
<td>0.92 um</td>
<td>1.63 um</td>
<td>2.1 um</td>
</tr>
<tr>
<td>s. dev.</td>
<td>0.29 um</td>
<td>0.34 um</td>
<td>0.59 um</td>
<td>x</td>
</tr>
<tr>
<td>count</td>
<td>10</td>
<td>9</td>
<td>13</td>
<td>3</td>
</tr>
<tr>
<td>core size</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>0.51 um</td>
<td>0.53 um</td>
<td>0.56 um</td>
<td>0.5 um</td>
</tr>
<tr>
<td>s. dev.</td>
<td>0.20 um</td>
<td>0.14 um</td>
<td>0.19 um</td>
<td>x</td>
</tr>
<tr>
<td>count</td>
<td>10</td>
<td>9</td>
<td>13</td>
<td>3</td>
</tr>
<tr>
<td>core vol. %</td>
<td>37.1</td>
<td>19.1</td>
<td>4.05</td>
<td>1.3</td>
</tr>
</tbody>
</table>

233
REFERENCES


4. E. Wainer et al., Electrical Reports, Titanium Alloy Manufacturing Division, National Lead Company, Niagara Falls, NY. Ten reports were issued from 1938 to 1943. The last three, No. 8 to 10 dealt specifically with titanates and their solid solutions.


