

Chapter 1

Introduction

1.1 Background

A dielectric is an insulating material used in electric circuits in the form of a capacitor. Ceramic capacitors are widely employed in electronic device having basic functions such as blocking, coupling, decoupling, AC-DC separation, filtering and energy storage. Ceramic capacitors are produced in wide range of compositions and shapes to cover all those applications. In the early days of electronics, steatite, glass and mica were widely used having low dielectric constant. Steatite was used as a substrate and to insulate the cross-over of conductors in hybrid circuits (1).

Dielectrics with high dielectric constants were produced commercially beginning with rutile ($K'=100$) in the 1930s and barium titanate ($K'=1500-2000$) in 1974. Nevertheless, these two materials had a high temperature coefficient of the dielectric constant. In addition, the other serious problem was the decrease of the dielectric constant in $BaTiO_3$ devices when they were subjected to a dc field. Also above the Curie temperature of $BaTiO_3$ (120-130 °C) the dielectric constant decreased making it improper for a high temperature capacitor. However, at present most of commercial dielectrics are based on barium titanate modified by altering the composition and by controlling ceramic textures to optimize the required properties.

The development of a capacitor has been concentrated on a size reduction and increasing the dielectric constant.

The capacitance of a parallel plate capacitor can be defined as the following equation.

$$C_A = \epsilon_0 K' / d$$

where C_A is the capacitance per unit area for a single parallel plate

ϵ_0 is the permittivity of free space

K' is the relative permittivity or relative dielectric constant

d is the thickness of the dielectric material

From this equation, there are two potential ways of increasing the capacitance per unit area: reducing the thickness and increasing the dielectric constant

1. Reducing the thickness

To reduce the thickness, the capacitors have to be fabricated by tape casting, a doctor-blade technique under 0.02 mm.(20 μm). To achieve a high capacitance, the dielectric thickness must be lower but such an extremely small thickness makes the fabrication processes limited and also affects the dielectric breakdown strength and capacitance sensitivity to working voltages. To avoid this problem is to construct the multilayer instead of reducing thickness.

2. Increasing the dielectric constant

After the discovery of the ferroelectric properties of BaTiO_3 it is found that BaTiO_3 has a high K' and many temperature ranges due to three phase transitions. In addition, its dielectric constant is sensitive to temperature change and dc field. That is, the dielectric constant rapidly decreases over Curie temperature (120–130 $^\circ\text{C}$). The research and development should be concentrated on the new materials to achieve a high dielectric constant over a sufficient temperature range. The aim of this thesis is to study a new dielectric material to be technically useful in high temperature dielectric device and also can be used near room temperature.

1.2 Possible Approaches and Requirements

The materials considered for modification of a new dielectric system for high temperature capacitors should have:

1. large dielectric constant (K'); commonly found in lead-based perovskite
2. multiple phase transitions; easily modified by adding dopants to broaden temperature dependence of K'
3. antiferroelectric phase; giving an increase in K' with increasing dc field
4. relaxor behavior; referring to as a "diffuse or broadened phase transition" (DPT)

Modified by adding cations as dopants, K' peak of the transition temperature can be shifted to within the working temperature region and distributed to the transition peaks so that K' is broad or flat. Relaxor materials may also be useful in developing a temperature stable dielectric. A number of solid solutions of complex compounds in the perovskite and tungsten bronze families show these diffuse phase transitions. The followings are physical phenomena (2) found in those compositions.

1. an unusual relaxation of dielectric polarization in the phase transition region
2. a dependence of the reciprocal dielectric constant (above the T_{\max}) on the square of temperature (3).

$$\frac{1}{K'} \propto (T - T_{\max})^2$$

where T_{\max} is the temperature of the K' maximum

3. a diffuse or broad dielectric constant maximum in transition region, which is strongly both frequency and temperature dependent.

There are certain properties which distinguish relaxor from normal ferroelectric and antiferroelectric concluded in Table 1 (4).

Table 1. Property difference between relaxor and normal perovskite ferroelectric and antiferroelectric (4).

Property	Normal	Relaxor
Permittivity temperature dependence; $\epsilon(T)$	Sharp 1 st or 2 nd order transition at T_c	Broad-diffuse phase transition about maxima (T_{max})
Permittivity temperature & frequency dependence; $\epsilon(T, \omega)$	Weak frequency dependence	Strong frequency dependence
High temperature dielectric response	Proportional to $\frac{1}{(T-T_0)}$	Proportional to $\frac{1}{(T-T_{max})^2}$
Diffraction of X-Ray	Line splitting owing to spontaneous deformation from paraelectric to ferroelectric or cell doubling for antiferroelectric	No X-Ray line splitting (pseudo-cubic)

The explanation for the broadening of K' of a relaxor is due to local variations in internal stress and composition in which the energy difference between two phases is small. All relaxors contain two or more species of ion on the same sites, as in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and it appears likely that their behavior arises from fluctuations in composition between microscopic regions. This process results in local variations of the Curie temperature and so accounts for the broad phase. It is believed that phase boundary and domain wall motion contribute to the frequency dependent K' . It has been found in the case of $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ that under suitable annealing conditions the ions on the B-sites become ordered instead of randomly distributed and thus the relaxor characteristics diminish as the degree of ordering increases (1). One method of broadening K' is to change the composition or form a solid solution encouraging random occupation of the same site with different cations. In order to support composition fluctuations or disorders, there are three principle methods by which the dielectric constant of a ferroelectric ceramic should be maximized over a wide range of temperature.

1. Charge difference on the same ion site

Large difference in the valence on the same site results in a strong tendency to order through electrostatic forces and thus eliminate the relaxor behavior.

2. Ion size

Materials with large size differences on the same site are driven towards ordering while materials with near identical cation size may stay disorderd.

3. Cation ratio

Some specific cation ratios on the same site can increase the degree of ordering.

In the solid solution it is possible for ion segregation (5) to occur. This will increase the compositional heterogeneity in various parts of the crystal and give rise to broadening of the phase transition.

Commercial compositions are usually complex mixtures prepared from binary solid solutions. However, they have a large dependence of dielectric constant on temperature. From the point of view of high capacitance, it would be useful if the maximum K' at the Curie temperature could be extended over a wide temperature range to attain a small dependence of the dielectric constant on the temperature.

The selection of a material to study as the base of a high temperature capacitor system, can be attained by preparing and testing various compositions. The starting candidate materials were selected from the literature (6,7). The criteria for this selection were low sintering temperature, good density, high K' with multiple and broad phase transitions up to at least 300 °C. Both the $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ (BNT) and $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3 - \text{PbTiO}_3$ (BNT-PT) base system gave a positive indication to further modify for a high temperature capacitor with a wide range of antiferroelectric phase.

1.3 Background of BNT and BNT-PT

$\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ was a complex compound with the perovskite structure (ABO_3). It was first synthesized by Smolenskii and Agranovskaya in 1959 (8). Subsequently, (9) BNT was found to be ferroelectric from the polarization–electric field hysteresis loop. From x-ray diffraction, its

structure was rhombohedral distortion having the lattice parameter of 3.891 \AA and $\alpha = 89^\circ 36'$ observed by Ivanova et al. (24) and determined by assuming a cubic structure.

In 1974 Sakata and Masuda (10) found that ferroelectric BNT transformed from ferroelectric to antiferroelectric above $220 \text{ }^\circ\text{C}$ and to paraelectric phase at $320 \text{ }^\circ\text{C}$ corresponding to the maximum dielectric constant. Above $320 \text{ }^\circ\text{C}$ the phase was tetragonal and changed to cubic phase above $520 \text{ }^\circ\text{C}$ with no detectable change in dielectric response (35). With an applied dc field of 2 kV/mm , not only K' increased in the range of $220 \text{ }^\circ\text{C}$ to $320 \text{ }^\circ\text{C}$ but the transition temperature at $220 \text{ }^\circ\text{C}$ also moved toward higher temperature. This result indicated that the phase between $220 \text{ }^\circ\text{C}$ and $320 \text{ }^\circ\text{C}$ was antiferroelectric. However, they could not detect the superlattice lines from x-ray diffraction. In addition, at this phase transition observed by Isupov and Kruzina (11), the character of domain structure was unchanged based on optical and neutron diffraction studies.

Zvirgzds et al. (12) investigated structural phase transition especially rhombohedral phase. The calculated lattice parameter was 3.8848 \AA and α was $89^\circ 54' \pm 1'$. The values of linear expansion coefficient calculated from the lattice parameter were $1.55 \times 10^{-5} \text{ K}^{-1}$ in the cubic phase and tetragonal phase, $1.05 \times 10^{-5} \text{ K}^{-1}$ in rhombohedral phase from 510 K to 390 K ($237 \text{ }^\circ\text{C}$ to $117 \text{ }^\circ\text{C}$) and $0.98 \times 10^{-5} \text{ K}^{-1}$ from 390 K to 290 K ($117 \text{ }^\circ\text{C}$ to $17 \text{ }^\circ\text{C}$). These results were different from those of Pronin (39) in that his values of linear expansion coefficient measured from a dilatometer were $0.64 \times 10^{-5} / ^\circ\text{C}$ in the tetragonal phase, $0.53 \times 10^{-5} / ^\circ\text{C}$ from $300 \text{ }^\circ\text{C}$ to $230 \text{ }^\circ\text{C}$ and $0.64 \times 10^{-5} / ^\circ\text{C}$ from $125 \text{ }^\circ\text{C}$ to room temperature.

The study of temperature dependence of the dielectric constant for BNT obviously showed two phase transitions, a hump around 220 °C and maxima of K' at 320 °C. There was no significant change at 540 °C (10,39). In contrast, the results for dielectric measurements given by Zvirgzds et al. (12) exhibited two K' peaks around 340 °C and 510 °C at a frequency of 1 kHz. Isupov (11) also had a peak of K' at 520 °C. After annealing at 800 °C for 8 hrs., however, this high temperature peak was absent. He assumed that this peak was associated with the presence of defects.

Studies of the dielectric properties as a function of temperature have shown that BNT commonly exhibits a broad maxima in the dielectric constant. In single crystal of BNT, its dielectric constant was reported differently depending on growing techniques, 16,000 from flux technique and 12,500 from Czochralski method, reported by Seung-Eek Park and Chung (13). A maximum K' approaching 4000 at a frequency of 1 kHz had been reported by Isupov and Kruzina (11). However, after annealing at 800 °C the K' decreased and Curie point decreased from 380 °C to 330 °C. Additionally, the frequency dispersion of $K'(T)$ also decreased. The reason given was from the presence of defects. In comparison, the results of K' obtained from BNT ceramics were similar in Smolenskii 's (9) and Sakata 's work (10,14). The maximum K' of 1 kHz was 2,300 at 320 °C. The dielectric loss increased rapidly above 300 °C. Thus, the K' and dielectric loss at a frequency of 1 kHz were measured only up to 400 °C.

In the case of piezoelectric (14,15) and pyroelectric (16) properties, BNT tends to be a desirable candidate for piezoelectric devices and pyroelectric radiation detectors. On account of unsuccessful poling, there was little information on these properties. After 1989, modified by Takenaka et al. (15,17), BNT was doped with 6.5% Sr and 6.5% Pb used in piezoelectric

application as ultrasonic transducers at high frequency with a low permittivity and a high electromechanical coupling factor. In pyroelectric applications, BNT was doped with 5% Sr and 5% Pb giving a large figure of properties which can be compared with PZT. Takenaka, Maruyama and Sakata (18) also prepared BNT doped with Ba for lead-free piezoelectric ceramics. Its morphotropic phase boundary (MPB) existed at $x = 0.06 \sim 0.07$ in $(\text{Bi}_{1/2}\text{Na}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) system. The composition at MPB is used in high frequency ultrasonic application and as piezoelectric actuator because of a lower permittivity and a high electromechanical coupling factor along with high mechanical strength.

In 1994, Kuharungrong (19) studied and developed BNT with Pb dopant for utilization at high temperature. It was found that 10% Pb doped BNT was the best composition in $(1-x)\text{BNT}-x\text{PT}$ system. In addition, a dielectric constant increased with increasing Pb and first transition lowered and broadened to get a wide range of temperature. At 17% Pb this composition was not suitable to be modified since the first transition was abruptly disappeared and the dielectric constant at room temperature also decreased. To improve this property at room temperature, Ba cation is considered as a dopant of BNT and $0.90\text{BNT}-0.10\text{PT}$ systems because BaTiO_3 has a high dielectric constant at room temperature. Although BaTiO_3 has a high temperature coefficient of dielectric constant, BNT doped with Ba is expected to give a broad transition temperature.

1.4 Objectives of this Thesis

Although BNT is a good candidate base material for high temperature capacitor, most studies on this material and its modification have focused on piezoelectric and pyroelectric applications. The aim of this work is to study

and investigate the effects of Ba on the dielectric properties and the microstructure of BNT and 0.90BNT-0.10PT systems. With regard to this aim, it is designed to make the systems useful as a high temperature dielectric capacitor.