CHARPTER I

INTRODUCTION

Rational for the study

Ferroelectric materials have been applied to many electronic and optical devices due to their excellent dielectric, piezoelectric and optical properties. $BaTiO_3$ (BT) has been the most widely studied for lead-free ferroelectric material. This material has shown typical interesting properties such as a large electromechanical coupling factor, high permittivity with an abrupt change near the Curie temperature and a low loss tangent [1]. Many efforts have been made to modify the dielectric properties of $BaTiO_3$ ceramics for typical applications. Substitution of isovalent ions for the host lattice cations in perovskite lattice plays a significant role in these modifications. Substitution of Zr^{4+}, Sn^{4+} for Ti^{4+} results in the formation of $BaZrO_3$ and $BaSnO_3$. These materials form solid solutions with $BaTiO_3$ and alter its structural features, resulting in a shift in phase transition temperature along with modified dielectric properties [2, 3, 4].

The $BaZr_xTi_{1-x}O_3$ (BZT100x) system is one of the first $BaTiO_3$-based which was studied widely due to their very high and broad dielectric constant, excellent tunability and because they are environmentally friendly materials [5]. The ferroelectric properties of these materials are largely dependent on the amount of Zr substitution [6]. Normal ferroelectric behavior and good dielectric properties, with the Curie temperature above room temperature, were exhibited when $0 < x < 0.2$. When $x > 0.3$, relaxor behavior was observed and the Curie temperature went below room temperature [7]. BZT100x with $x = 0.1$ (abbreviated as BZT10) ceramic is very interesting due to its high dielectric constant, low dielectric loss, wide dielectric curve and a Curie temperature above room temperature [7, 8]. However, the preparation processes for synthesizing this ceramics requires high energy while the products frequently showed low quality [8]. Preparation via the wet chemical route such as the sol-gel route or hydrothermal method could solve these problems, but these techniques require a longer processing time, require expensive chemicals, special equipment and have a complex procedure [7, 9]. Therefore, the study of new ways of synthesizing BZT10 which consists of low energy consumption, uncomplicated and produced high quality products is interesting.

For BZT100x with $x \leq 0.15$, it has been observed from the published literature that zirconium content substitution highly influences phase transition characteristics and electrical properties of a BZT system. However, there are several different reports about the effects of zirconium substitution on the phase formation and dielectric properties of BZT [6, 8, 10]. Hence, the fabrication of high quality BZT100x ceramics ($0.025 \leq x \leq 0.150$) via the combustion technique for investigating the effects of zirconium content on the phase formation and dielectric properties of BZT is an attractive topic.

Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) is a promising perovskite structure lead-free ferroelectric material. This compound has a large remanant polarization (P_r) of 38 μC/cm^2 with a coercive field (E_c) of 73 kV/cm at room temperature [11]. However, the dielectric properties and the piezoelectric properties of BNT ceramics are significantly lower than the lead-based ceramics [11]. To further improve its properties, a modified BNT composition with some cation dopants has been selected as a substitute for A- site of the perovskite lattice. Lu, et al. [12] investigated on Li and K substituted at the A-site of the BNT lattice. For $Bi_{0.5}(Na_{0.74}K_{0.16}Li_{0.10})_{0.5}TiO_3$ (BNKL1610), the piezoelectric constant d_{33} and electromechanical coupling coefficient K_p are 160 pC/N and 0.35, respectively, which are a great improvement compared with pure BNT ceramics. However, BNT and BNT-based ceramics are usually synthesized through the solid-state reaction method [13]. High firing temperature on preparation processing causes the raw materials to vaporize, which induces the formation of a secondary phase [14]. The secondary phase formation decreases the electrical properties of the prepared ceramics. Hence, the synthesis of BNKLT1610 via the special technique, which requires low firing temperature, is an attractive area of investigation. Moreover, the effects of firing temperatures on phase formation and electrical properties of BNKLT1610 need to be studied.

Some cation substituted at the A-site lattice, binary system of BNT-based such as BNT-BT [15], BNT-KNN [16] and BNT-BZT [17, 18] is effective technique in improving unsatisfactory properties of BNT ceramics. For example, Parija, et al. [19] demonstrated that doping BZT for 5 mol% to BNT enhanced the ε_m from 1020 to 3533, d_{33} from 41 to 131 pC/N and P_r from 2.5 to 12 $\mu C/cm^2$. This can be attributed to the addition of BZT into the BNT system which induced the morphotropic phase boundary (MPB) of rhombohedral and tetragonal phases. This greatly enhanced the electrical properties of the system. Therefore, the idea of the cation substituted at the A-site lattice and the binary system of BNT-based solid solution to improve BNT properties by forming a new system of BNKLT-BZT is greatly interesting.

Recently, the combustion technique has become an attractive technique to prepare high quality ferroelectric ceramics [20, 21, 22, 23, 24]. This technique is modified from the solid-state reaction technique and the process yields reactive powders with high purity, more homogeneous, fine particle size and lower firing temperature compared with the powders prepared via the solid-state method. The energy released from the decomposition reaction of fuel speeds up the chemical reaction of raw materials. Moreover, the liquid phase caused from the melting of fuel creates an easier chemical reaction of raw materials.

In this work, BZT100x with $0.025 \leq x \leq 0.150$, BNKL1610 and BNKLT1610-xBZT with $0.025 \leq x \leq 0.150$ ceramics were synthesized via the combustion technique. In the case of BZT100x, the composition of $x = 0.10$ was selected to study the effects of firing temperatures and dwell time on phase formation, microstructure and dielectric properties. Thereafter, the study of BZT100x with $0.025 \leq x \leq 0.150$ focused on the effects of zirconium content on the phase formation, microstructure, phase transition characteristics, dielectric properties and ferroelectric properties. For BNKLT1610 synthesizing, the phase formation, microstructure and dielectric properties, which were affected by firing temperatures in the preparation processes, were also studied. Then, new kinds of BNKL1610-xBZT solid solution were synthesized via the combustion route. The study placed special emphasis on the effects of BZT content on phase formation, microstructure and dielectric properties.

Objectives of the study

The aim of this study was the preparation of BZT100*x*, BNKLT1610 and BNKLT1610-*x*BZT ceramics through the combustion technique. Special emphasis was placed on the following:

1. To study the effects of firing conditions on phase formation, microstructure and the dielectric properties of BZT10 ceramics prepared via the combustion route.

2. To study the effects of composition on phase formation, microstructure, dielectric properties, phase transition behavior and ferroelectric properties of the BZT100*x* ceramics with $0.025 \leq x \leq 0.150$ ceramics synthesized via the combustion route.

3. To study the effects of firing temperature on phase formation, microstructure and dielectric properties of BNKLT1610 ceramics synthesized through the combustion technique.

4. To study the effects of composition on phase formation, microstructure and dielectric properties of BNKLT1610–*x*BZT with $0.025 \leq x \leq 0.150$ ceramics prepared via the combustion technique.

Expected outputs of the study

1. To understand the effects of firing conditions on phase formation, microstructure and dielectric properties of BZT10 ceramics prepared via the combustion route.

2. To understand the composition affects on phase formation and electrical properties of the BZT100*x* ($0.025 \leq x \leq 0.150$) ceramics.

3. To understand the effects of firing temperature on phase formation, microstructure and dielectric properties of the BNKLT1610 ceramics synthesized via the combustion technique.

4. To understand the effects of BZT content on phase formation, microstructure and dielectric properties of the BNKLT1610–*x*BZT with $0.025 \leq x \leq 0.150$ ceramics prepared via the combustion technique.