CHAPTER 1

Introduction

1.1 Overview

Relaxor ferroelectric materials were first found in a perovskite soild solution compound of $Pb(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}O_3$ (PMNT) that shows good dielectric and electrostrictive properties at room temperature [1,2]. Their applications are related to converting mechanical energy into electrical form and vice versa [3,4]. However, Pb-containing compounds have recently been under restricted use in some countries due to health and environmental concerns. Therefore, the increasing of the studies in lead-free relaxor ferroelectrics which included $BaTiO_3$-$BaSnO_3$, the first binary system that exhibits relaxor behavior, 0.85BaTiO3-0.15BiAlO3 [5], $K_{0.5}Na_{0.5}NbO_3$-$SrTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ and $Ba_{0.92-x}Ca_{0.08}Nd_x(Zr_{0.18}Ti_{0.815}Y_{0.0025}Mn_{0.0025})O_3$ [4]. The unusual properties of relaxor ferroelectrics have attracted continued interest until now [6, 7]. Several features that indicate relaxor behavior include a broad dielectric permittivity peak, a shift of temperature at maximum dielectric constant with increasing frequency, slim ferroelectric hysteresis at room temperature and large strains [8, 9, 10, 11]. The origin of these unique properties has been proposed by several models such as superparaelectric model, dipolar glass model and random field model [12]. The latest model which attempts to explain relaxor phenomenon is soft polar nano region model discovered by Bokov and Ye [8]. The origin of the relaxor ferroelectric materials have been described by polar nano-regions (PNRs) which nucleated as material was cooled down below the Burn's temperature (T_B) [13, 14]. The size and number of the PNRs grew with decreasing temperature, leading to an increase in dielectric permittivity. The temperature continued to decrease, the dynamic of PNRs slowed down and led to a decrease in dielectric permittivity thus showing the maximum dielectric permittivity at maximum dielectric temperature (T_{max}). Finally, the dynamic of PNRs was frozen with further decreasing the temperature and was this point called the freezing temperature (T_{VF}) [11]

One of the promising lead-free relaxor ferroelectric ceramics, i.e. $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) originally found by Liu and Ren[15], showed exceptionally good piezoelectric properties but the synthesis and fabrication process involved rather high calcination (1300°C) and sintering temperatures (1550°C) [15,16]. It is believed that a use of nano-sized particles, which have a high energy surface area, could further improve the densification at low sintering temperature [18]. Therefore, in this work, the BCZT powder was synthesized by the sol-gel auto combustion method which could reduce the calcination temperature due to the nano-sized morphology of produced particles [19] There are many studies attempted to dope some oxides such as CuO [17] or co-doping with Bi_2O_3 and CuO [12] into BCZT to reduce the sintering temperature. Bi_2O_3 was often used as a sintering aid during ceramic fabrication since this compound was found to effectively reduce the sintering temperature in $BaTiO_3$ and BCZT system [20, 21]. The addition of Bi_2O_3 powder was in the range of 0.05 – 1.0 mol% in BCZT ceramics could reduce sintering temperature from 1550 to 1350°C by solid state route. The part of Bi^{3+} incorporated into B-sites of BCZT structure and the results showed the relaxor-like behavior for 1 mol% Bi_2O_3. The Bi_2O_3 addition affects the long-range ferroelectric order for the case of large doping amounts [22]. Beside they use Bi_2O_3, was found to affect dielectric and ferroelectric properties of relaxor compounds [20, 21]. In these studies, effects of Bi_2O_3 seemed to play a main factor in improving the physical and other related properties. It is expected that the addition of the Bi_2O_3 powder in lower content than previous works will improve the physical, ferroelectric and dielectric properties of the BCZT-*x*Bi ceramics

Moreover, in the last decade, many studies have been carried out in order to develop advanced electrical ceramics containing less or no lead. Particularly, the study of 0-3 ceramic composites between lead-based and lead-free components has led to promising results [23]. In order to achieve true synergetic effects of piezoelectric composite, in this study, we investigate for the first time the preparation and characterization of lead-free ceramics embedded with millimeter-sized lead-based single crystals. The lead-free BCZT-based composition has been chosen for the optimum condition from Bi_2O_3 additions. Various amounts of PMNT single crystals were used as the embedded phase to form 0-3 connectivity with the matrix. The microstructure of these ceramic matrix composites and their dielectric and ferroelectric properties were characterized as a function temperature and discussed in relation to their compositions. The author hopes that knowledge and understanding obtained from this research will lead to more fabrication of the 0-3 ceramic matrix composites with excellent physical and electrical properties.

1.2 Objectives of this work

In this research, the BCZT powder was synthesized by sol-gel auto combustion method. It was believed that this method could reduce calcination and sintering temperatures. A different amount of Bi_2O_3 powder was added into BCZT ceramic. It has been reported that Bi^{3+} ions could reduce sintering temperature and enter into the perovskite structure which is worth further investigation about the relationship between the structure and electrical properties. Moreover, the microstructure design of the 0-3 ceramic matrix composites could contributed to an enhancement of relaxor ferroelectric behavior, leading to high quality ceramics with good electrical properties. Therefore, this research aims to,

1. synthesize BCZT powder by sol-gel auto combustion method.
2. prepare BCZT with Bi additions.
3. prepare the 0-3 ceramic matrix composites with PMNT crystal additions.
4. investigate the effect of sintering temperature on microstructure and electrical properties of the BCZT ceramics.
5. investigate the effect of Bi addition on microstructure and electrical properties of the BCZT-*x*Bi ceramics.
6. investigate the effect of PMNT crystal addition on microstructure and electrical properties of the BCZT-*x*Bi-*y*PMNT ceramics.