

CHAPTER 1

INTRODUCTION

1.1 Background

Perovskite structure ferroelectric materials have been of great interest among materials scientist for almost century. The successful of the related research works have been performed in new materials, discovery of new properties and achievement of developed technology for applications [1]. Although they were initially developed for military purposes, then These applications are used in daily life thorough high complicated technology in industrial, medical devices, and high level research, for the applications such as, electrical, telecommunications, computing, aerospace, microelectronics, radio technology, laser technology and microwave devices [2]. The material with a high dielectric constant ($\epsilon_r \geq 1,000$) is called high dielectric materials or giant dielectric materials. Normally, many giant dielectric materials have a perovskite crystal structure. The perovskite material with dielectric constant more than 1,000 can be divided into two groups. The first group is normal-ferroelectric, e.g. $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) [3] and BaTiO_3 [4]. In this group, the materials show the permanent electric dipole moment, when the materials were placed in electric field and the electric dipoles are aligned along the direction of the external electric field. This effect leads to the dielectric response. The second is relaxor-ferroelectric, e.g. $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) [5], $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) [6], $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST) [7] and $(\text{Bi},\text{Sr})\text{TiO}_3$ [8]. These materials have electrical responsiveness at low temperature and under high electric field. It should be noted that many high dielectric materials are lead based materials. These lead based materials are not environmental friendly due to the volatility of lead at high processing temperatures. This motivates the searching for lead free (Pb) materials which have dielectric properties comparable or higher than the standard lead based

materials. Recently, the materials which exhibit high dielectric constant and scanty change when the temperature and frequency changes are wildly investigated. These materials consist of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) [9], $\text{K}_x\text{Ti}_y\text{Ni}_{1-x-y}\text{O}$ (KTNO) [10], CuO [11] and $\text{A}(\text{Fe}_{1/2}\text{B}_{1/2})\text{O}_3$ (A=Ba, Sr, Ca and B=Nb, Ta, Sb) [12]. It is noted that many large dielectric constant materials have similar dielectric behavior, i.e., they all exhibit a Debye-like relaxation and their dielectric constants are nearly independent of frequency and temperature below the transition temperature [13]. Usually large dielectric constants are found in ferroelectric materials and are related with atomic displacements of the non-centro symmetrical structure [13]. However, the complex perovskite of $\text{A}(\text{Fe}_{1/2}\text{B}_{1/2})\text{O}_3$ (A=Ba, Sr, Ca and B=Nb, Ta, Sb) is non-ferroelectric but exhibit high dielectric constant. Accordingly, the origin of the giant dielectric constant has been attributed to an extrinsic mechanism such as point and extended defects, contaminants, domain boundaries in grains boundaries, grains, non-ohmic electrode contacts, and surface layers. The extrinsic mechanism has been observed in many ceramics. All of these extrinsic effects have been reported

to lead to higher than expected permittivity values in many oxide-based ceramics. High dielectric materials have high loss tangent which is unsuitable for capacitor applications. To reduce the loss tangent, many attempts have been made such as forming some solid solutions between the high dielectric materials with other materials or doping with some elements [3, 10]. Furthermore, some high dielectric materials require a high temperature processing which causes high processing cost and results in the global warming effect. Attempt to reduce the temperature processing is an interesting aspect for the high dielectric materials research now.

In this work, some interesting ABO_3 perovskite structure materials such as $\text{SrFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (SFN) and BiFeO_3 (BFO) ceramics will be synthesized. Some elements such as Ho and/or Sb will be doped into the studied ceramics to improve their properties, especially for lowering the loss tangent. Furthermore, some alternative methods for synthesis the materials will be developed to reduce the temperature of the processing. Properties of the studied materials will be investigated with various

techniques. The electrical properties will be discussed in terms of microstructure and related with MW model.

1.2 Research objectives

The objectives of this study are as follows:

- 1.2.1 To investigate the electrical properties of $\text{Sr}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ and BiFeO_3 doped with Ho and/or Sb
- 1.2.2 To study the effects of method of synthesis on phase formation, microstructure and electrical properties of the studied materials.
- 1.2.3 To obtain new materials which have high electrical performance.

1.3 Usefulness of the research

The main education advantages of this work are:

- 1.3.1 To obtain knowledge for perovskite ceramics, multiferroic and the giant dielectric materials.
- 1.3.2 To obtain alternative methods for improvement of electrical properties of the SFN and BFO ceramics.
- 1.3.3 To obtain high performance properties of the studied materials for the capacitor applications.

1.4 Reference

- [1] G. M. Haertling, "Ferroelectric Ceramics: History and Technology," Journal of the American Ceramic Society, Vol. 82, 1999, Page No. 797-818.
- [2] A.J. Moulson, and J.M. Herbert, "Electroceramics: materials, properties, applications," Chapman and Hall, New York, 1990, ISBN: 0471-49747-9.
- [3] V. Bobnar, M. Hrovat, J. Holc, M. Kosec, "Giant dielectric response in $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3\text{-Pb}_2\text{Ru}_2\text{O}_{6.5}$ all-ceramic percolative composite," Applied Physics Letter, Vol. 92, 2008, Page No. 182911.

- [4] M. T. Buscaglia, M. Viviani, V. Buscaglia, L. Mitoseriu, A. Testino, P. Nanni, Z. Zhao, M. Nygren, C. Harnagea, D. Piazza and C. Galassi, "High dielectric constant and frozen macroscopic polarization in dense nanocrystalline BaTiO₃ ceramics," *Physical Review B*, Vol. 73, 2006, Page 064114.
- [5] V. V. Shvartsman and A. L. Kholkin, "Investigation of the ferroelectric-relaxor transition in PbMg_{1/3}Nb_{2/3}O₃-PbTiO₃ ceramics by piezoresponse force microscopy," *Journal Applied Physics*, Vol. 108, 2010, Page 042007.
- [6] I. Grinberg and A. M. Rappe, "Local structure and macroscopic properties in PbMg_{1/3}Nb_{2/3}O₃-PbTiO₃ and PbZn_{1/3}Nb_{2/3}O₃-PbTiO₃ solid solutions," *Physical Review B*, Vol. 70, 2004, Page 220101.
- [7] V. Bovtun, V. Porokhonsky, J. Petzelt, M. Savinov, J. Endal, C. Elissalde and C. Malibert, "Microwave Dielectric Properties of the Ordered and Disordered Pb(Sc_{1/2}Ta_{1/2})O₃ Ceramics," *Ferroelectrics*, Vol. 238, 2000, Page 17-24.
- [8] A. Chena, Z. Yua, J. Scottb, A. Loidlc, R. Guoa, A. S. Bhallaa and L. E.Crossa, "Dielectric polarization processes in Bi:SrTiO₃," *Journal of Physics and Chemistry of Solids*, Vol. 61, 2000, Page 191-196.
- [9] K. D. Mandal, A. K. Rai, L. Singh and O. Pakash, "Dielectric properties of CaCu_{2.9}Co_{0.1}Ti₄O₁₂ and CaCu₃Ti_{3.9}Co_{0.1}O₁₂ ceramics synthesized by semi-wet route," *Bulletin of Materials Science*, Vol. 35, 2012, Page 433-438.
- [10] P. K. Jana, S. Sarkar and B. K. Chaudhuri, "Low loss giant dielectric and electrical transport behavior of K_xTi_yNi_{1-x-y}O system," *Applied Physics Letters*, Vol. 88, 2006, Page 182901.
- [11] M. Li, A. Feteira and D. C. Sinclair, "Relaxor ferroelectric-like high effective permittivity in leaky dielectrics/oxide semiconductors induced by electrode effects: A case study of CuO ceramics," *Journal Applied Physics*, Vol. 105, 2009, Page 114109.
- [12] I. P. Raevski, S. A. Prosandeev, A. S. Bogatin, M. A. Malitskaya and L. Jastrabik, "High dielectric permittivity in AFe_{1/2}B_{1/2}O₃ non ferroelectric perovskite ceramics (A=Ba, Sr, Ca; B=Nb, Ta, Sb)," *Journal Applied Physics*, Vol. 93, 2003, Page 4130.

- [13] J. Liu, C. Duan, W. N. Mei, R. W. Smith and J. R. Hardy, “Dielectric properties and Maxwell-Wagner relaxation of compounds $ACu_3Ti_4O_{12}$ (A= Ca, $Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$),” Journal Applied Physics, Vol. 98, 2005, Page 093703.



ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved