CHAPTER I
INTRODUCTION

1.1 Principle and reason

In recent years, high-permittivity dielectric materials have been playing a significant role in microelectronic applications such as capacitors and memory devices (Homes et al., 2001). The microelectronic devices have been being driven to nanoelectronics by an almost insatiable appetite for smaller and faster devices (Saha et al., 2006). In memory devices (e.g., static and dynamic random access memories), based on capacitive components, the static dielectric constant of a material will ultimately decide the degree of miniaturization (Scott, 1998). The dimension of the memory devices can, therefore, be miniaturized by increasing the dielectric constant of the dielectric layers in the devices. Normally, high-permittivity dielectric materials with a static dielectric constant value above 10^3 consist of ferroelectric oxide and relaxor oxide such as $BaTiO_3$ and $PbMg_{1/3}Nd_{2/3}O$ (Cross, 1987; Viehland et al., 1991; West et al., 2004). However, both classes of materials exhibit the large variation of their dielectric constant with temperature, which is undesirable for many applications. For example, stably static dielectric constant values of dielectric layers in capacitors are needed for fabrication of the high performance devices, which can operate properly under a variety of conditions. Thus, if the static dielectric constant is unstable and depends strongly on temperature, the devices will not be robust and may fail. Moreover, most such classes of materials contain lead, which is not environmental-friendly (Wu J et al., 2002). Consequently, the lead-free dielectric material with high dielectric constant and thermally stability is needed for future electronic applications.

Recently, J Wu et al. (2002) have reported a giant dielectric response in, a non-perovskite and non-ferroelectric material, Li and Ti co-doped NiO ($Li_xTi_yNi_{1-x-y}O$ (LTNO)) ceramics. In general, the static dielectric constant of NiO ceramic is about 30 at room temperature (Lin et al., 2004; 2005b). However, the dielectric constant of the NiO ceramic could be enhanced by co-doping with Li and Ti ions. The dielectric constant values of the LTNO ceramics were found to be about 10^3–10^5 with nearly temperature independent in the range of 200-450 K, depending on Li and Ti doping concentrations (Wu J et al., 2002; Deng, Nan, 2005). Interestingly, the dielectric and electrical properties of the LTNO ceramics could be tuned by changing the concentration of the Li and Ti dopants (Wu J et al., 2002; Deng, Nan, 2005; Lin et al., 2005b; Lin et al., 2006a). As a result, it is now believed that the LTNO ceramic is a promising material system for future electronic applications. By using an impedance spectroscopy combined with microstructure and phase composition analyses, it was proposed that the LTNO ceramics exhibited a core/shell microstructure, consisting of the insulating shell of Ti-rich boundaries and the semiconducting particle grains of Li-doped NiO (Deng et al., 2003; Wu J et al., 2003; Lin et al., 2006a). Consequently, the giant dielectric properties of the LTNO ceramics were suggested to be attributed to an internal barrier layer capacitor (IBLC) effect based on the Maxwell-Wagner polarization (interfacial polarization) mechanism. With applying an electric field across the LTNO ceramics, the movement of charge carriers inside the semiconducting core grains is blocked by the insulting barriers at the grain boundary shells. These accumulated charges at the grain boundaries can induce the interfacial polarization at the interface between the grains and grain boundaries. As a result, the giant dielectric response in the LTNO ceramics is therefore attributed to the Maxwell-Wagner polarization at the grain boundaries of the LTNO ceramics.

Besides the LTNO system, the giant dielectric properties of other NiO-based ceramic systems have also been reported such as $Li_xAl_yNi_{1-x-y}O$ (Lin et al., 2004), $Li_xSi_yNi_{1-x-y}O$ (Lin et al., 2005a), $Li_xTa_yNi_{1-x-y}O$ (Hsiao et al., 2007), $Li_xV_yNi_{1-x-y}O$ and $Li_xW_yNi_{1-x-y}O$ (Chen GJ et al., 2009), $K_xTi_yNi_{1-x-y}O$ (Jana et al., 2006; Jana et al., 2007a,b,c,d), $Na_xTi_yNi_{1-x-y}O$ (Jana et al., 2008), $Na_xAl_yNi_{1-x-y}O$ (Manna et al., 2008), $Mg_xTi_yNi_{1-x-y}O$ and $Y_xTi_yNi_{1-x-y}O$ (Cheng et al., 2008), $Li_xZr_yNi_{1-x-y}O$ (Manna, De, 20010), and $Zr_xNi_{1-x}O$ (Chen K et al., 2007) ceramics. Unfortunately, the loss tangent (tanδ) of these material systems is still too large (much larger than 0.05), which is the major obstacle for their applications. Furthermore, the explanation of the giant dielectric behavior of these NiO-based ceramic systems is still unclear and uncompleted. Hence, it is important to seek a low loss giant dielectric ceramic of

NiO-based systems. Most importantly, the giant dielectric and the polarization relaxation behavior of these ceramics must be clarified.

In this thesis, ***A*** and ***B*** co-doped NiO ceramics (***A***=Li and ***B***=Ti, Al, V, and Fe) with different concentrations of the ***A*** and ***B*** dopants are synthesized with several methods. The phase composition and microstructure are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS), respectively. The dielectric properties and related electrical response of the sintered NiO-based ceramics are investigated as functions of temperature, frequency, and dc bias. Moreover, the effects of heat treatment on the dielectric properties are also studied.

1.2 Objectives of the research

The objectives of this research are as follows:

1.2.1 To synthesize the ***A*** and ***B*** co-doped NiO ceramics (where ***A***=Li and ***B***=Ti, Al, V, and Fe).

1.2.2 To characterize the microstructure and phase composition of the synthesized NiO-based ceramics.

1.2.3 To study the dielectric and electrical properties of these NiO-based ceramics as functions of frequency, temperature, and dc bias.

1.2.4 To explain the mechanism of the giant dielectric behavior of the NiO-based ceramics and to exclude the important factors that have an influence on their dielectric properties at the different frequency ranges.

1.3 Limitations of study

1.3.1 Synthesis of the ***A*** and ***B*** co-doped NiO (where ***A***=Li and ***B***=Ti, Al, V, and Fe) ceramics.

1.3.2 Study of microstructure and phase composition of the synthesized NiO-based ceramics by using the XRD, SEM, and EDS techniques.

1.3.3 Study of the dielectric and electrical properties of the synthesized NiO-based ceramics at various frequencies, temperatures, and dc bias voltages.

1.3.4 Investigation of the interfaces and heat treatment effects on the dielectric properties of the synthesized NiO-based ceramics.

1.4 Location of the research

1.4.1 Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand, 40002

1.4.2 National Metal and Materials Technology Center (MTEC), Thailand Science Park, 114 Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120

1.4.3 Thai Microelectronics Center (TMEC) 51/4 Moo 1 Suwintawond Road, Wangtakien, Muang, Chachoengsao 24000, Thailand

1.5 Anticipated outcomes

1.5.1 Novel syntheses of the giant-permittivity NiO-based ceramics with very good dielectric properties using several routes.

1.5.2 The most possible mechanism(s) of the origin of giant dielectric response in the NiO-based ceramics.

1.5.3 International publications.

1.6 Structure of thesis

The structure of the thesis consists of six chapters. Chapter I, introduction, introduces an overview of this thesis as described above. Chapter II, theoretical background, provides theoretical background for dielectric properties and electrical responses in materials; several models of polarizations and dielectric relaxations are included in this chapter as well. Chapter III, literature review, reviews the researches related to the giant dielectric properties of the NiO-based ceramics as well as the controversy for the origin of their giant dielectric response. Chapter IV, research methodology, introduces the preparation and characterization of the NiO-based powders and ceramics including the dielectric and electrical measurement. The crystal and microstructural characterization analyses as well as the dielectric and electrical measurement are also summarized in this chapter. Chapter V, results and discussion, presents the experimental results and interprets these results to discuss the possible mechanism(s) of the observed dielectric and electrical properties. Finally, Chapter VI, conclusions and suggestions, summarizes the experimental results and the brief discussion; moreover, it provides the useful suggestions to improve the work for future researches.