CHAPTER 1

INTRODUCTION

Lead–based complex perovskites have been matured and are accepted by materials scientists as being critical to the success of ferroelectric ceramics which are in service throughout the world.[1-5] They have been introduced to replace the representative of normal ferroelectric barium titanate ($BaTiO_3$) mainly because of their lower firing temperature, higher dielectric constant, and broader dielectric peak, which are desirable features for wide range of applications (Fig. 1.1).[2, 7] Among the lead–based complex perovskites, lead zirconate titanate ($Pb(Zr,Ti)O_3$ or PZT) and lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$ or PMN) have been investigated extensively, both from academics and commercial viewpoints.[2, 8]

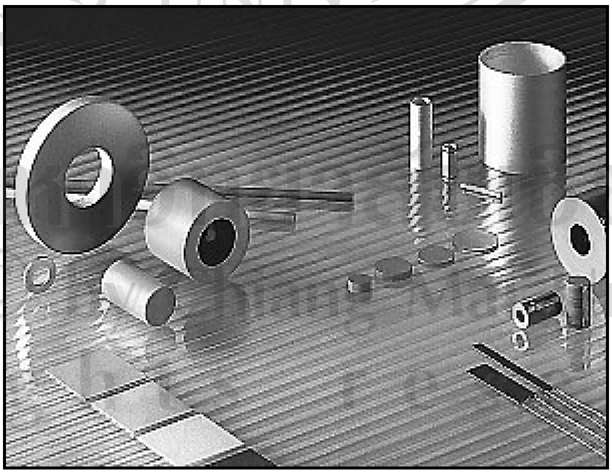

Fig. 1.1 Variety of ferroelectric ceramics used in piezoelectric and electrostrictive applications, such as actuators, sensors and capacitors.[9]

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These two compounds are probably best known for their ferroelectric, piezoelectric and dielectric properties. Especially, PZT ceramic (the prototype of piezoelectrics) has attracted the intention with its dominant piezoelectric properties which are suitable for the applications in area of transducers, electromechanical sensors and actuators, etc.[10] One of the most important characteristic features of the phase diagram for this $Pb(Zr_xTi_{1-x})O_3$ system is the existence of nearly temperature-independent phase boundary around $x = 0.5$ which separates a rhombohedral Zr-rich phase from a tetragonal Ti-rich phase.[11] The dielectric constant, piezoelectric constant and electromechanical coupling coefficient all exhibit a pronounced maximum value for the composition corresponding to this phase boundary, which is generally referred to as the morphotropic phase boundary (MPB). The compositions close to the MPB have been extensively exploited in commercial.[11] In practice, the Curie temperature or T_c of $Pb(Zr_{0.52}Ti_{0.48})O_3$ is ~ 380 °C.[4, 11-14] This is leading to a high working temperature for PZT but the consistency is only on a narrow range of temperature.

Lead magnesium niobate (PMN) is nowadays acknowledged as the prototype of relaxor ferroelectrics which are suitable for capacitors, actuators and electro-optics applications.[8, 15-17] This compound exhibits a broad range transition of dielectric constant, with temperature as a function of frequency, in its maximum dielectric constant. However, a practical limitation to the utilisation of this compound in device applications has been the lack of a simple, reproducible preparation technique for a pure perovskite phase with consistent properties. The formation of PMN is often accompanied by the occurrence of undesirable pyrochlore phases, which significantly degrades the dielectric properties of PMN-based ceramics.[16-18]

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There are several different preparation techniques that can be utilized to fabricate high-purity PMN powders.[16-19] A breakthrough was made in 1982 by Swartz and Shrout[19] who introduced a two-step process to PMN synthesis bypassing the formation of pyrochlore phases, called the *Columbite method*. In this process, the constituents MgO and Nb_2O_5 are first mixed and reacted together to form magnesium niobate ($MgNb_2O_6$), prior to mixing and reacting with PbO in the second step of calcination at elevated temperature. Interestingly, the same method has not been widely applied to the preparation of PZT. Moreover, the optimisation of firing conditions used in the mixed oxide process has not been paid attention, and the effects of applied dwell time and heating/cooling rates have not yet been studied extensively. As an extension of the research on the PZT powder preparation, in this work, an attempt has been made to synthesis and to investigate the PZT powders by employing an intermediate phase of zirconium titanate ($ZrTiO_4$) as a key precursor.

Generally, dielectric properties of the PZT and PMN ceramics are strongly dependent on processing history. The recurrent theme of many research works has been focused on the study of the dependence of processing parameters on microstructure and electrical response.[15, 16] Many details of these compounds have not been fully evaluated and developed as possible base compositions for further electroceramic utilizations. For further connection, the solid solutions between PZT and PMN are expected to synergetically combine the properties of both normal ferroelectric PZT and relaxor ferroelectric PMN.

In this study, the compositions in the PZT–PMN systems have been developed based on the simple approach of solid-state reaction. This project involves a production of high purity PZT, PMN and their solid solutions in both powder and

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ceramic forms. The effects of processing variables on the microstructure and dielectric properties have been evaluated, in order to develop a comprehensive understanding on lead-based complex perovskites.

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