# CHAPTER I

# INTRODUCTION

## 1.1 Background

A ferroelectric material is the one that has a spontaneous polarization (Ps) in crystal, the first discovered in Rochell salt ($KNaC_4H_4O_6.4H_2O$) by Valesek in 1920. A wide range of materials exhibits the ferroelectric behavior, ranging from inorganic crystals (potassium dihydrogen phosphate) to organic crystals. The most widely used ferroelectric materials are oxides of single crystal and ceramic materials that have perovskite structure, such as barium titanate and *lead zirconate titanate (PZT)*. In this research work preparation of lead zirconate titanate $Pb(Zr,Ti)O_3$ was studied using titanium glycolate, zirconium glycolate and lead glycolate as precursors.

Lead zirconate titanate, a binary suspension solution of $PbTiO_3$ and $PbZrO_3$, is a ferroelectric and piezoelectric material. The structure of PZT is a perovskite $ABO_3$ structure, as shown in Figure 1.1 (Jaffe *et al.*, 1971). The depends on temperature and the composition of the partial substitution of Zr for Ti in PZT, as shown by the PZT phase diagram in Figure 1.2 (Jaffe *et al.*, 1971).
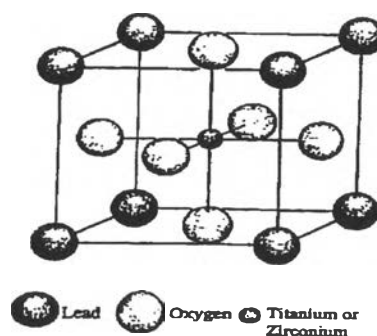


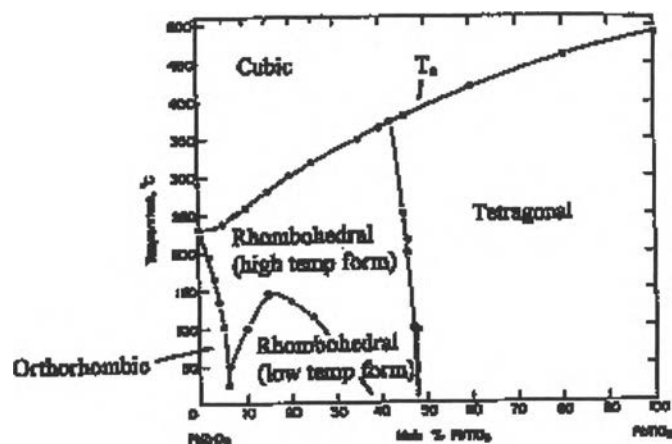Figure 1.1  The PZT cubic perovskite structure.

Figure 1.2 The phase diagram of PZT.

The composition of the partial substitution of Zr for Ti in PZT is called the morphotropic phase boundary (MPB) of PZT [Pb(Zr$_x$ Ti$_{1-x}$)O$_3$] having a finite range of x (where x is 0.52-0.55) and exhibiting high dielectricity and high electromechanical coupling coefficients (Dage *et al.*, 1997). The most useful PZT compositions are located at the phase boundary near 47 mole percent of PbTiO$_3$ (Suzuki *et al.*, 1996). This particular phase boundary is called morphotropic phase, meaning that the transition between tetragonal and rhombohedral PZT phases occurs at essentially the same composition, regardless of the temperature (Swartz and Wood, 1991). In addition, the temperature to control the pure perovskite phase structure is very important (Park *et al.*, 2001).

The formation of the perovskite structure:

$$ A \xrightarrow{\;\;k_1\;\;} Py \xrightarrow{\;\;k_2\;\;} Pe \qquad (1.1) $$

where A, Py and Pe represent amorphous pyrochlore and perovskite phases. Each step uses kinetic energy (k$_1$ and k$_2$) to change the structures. The activation energy calculated for perovskite formation was 26 kJ/mol (Chen and Mackenzie, 1990). The relative amounts of perovskite and pyrochlore phases are determined by measuring the relative intensity of XRD peaks and using the following equation (Lee *et al.*, 2002).

$$\% \text{ perovskite content } = \frac{I_{111}(Pe)}{I_{111}(Pe) + I_{222}(Py)} \quad (1.2)$$

Lead zirconate titanate ceramics have found widespread applications because of their superior properties :

1.  High Curie points (about 350°C) that allow for relatively high maximum temperature use.
2.  Possibly high poling efficiencies.
3.  Extremely large piezoelectric coefficients and coupling factors.
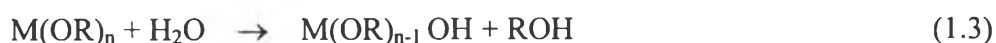4.  Relatively easy tailoring of properties via compositional modification.

PZT has been prepared using various methods, viz. mixed oxide powder, co-precipitation and sol-gel process. Although the sol-gel process has many advantages, such as providing molecular homogeneity, easiness in controlling the chemical composition, and low processing temperature, not many works have succeeded in eliminating the moisture sensitivity and lowering the cost of the precursors.
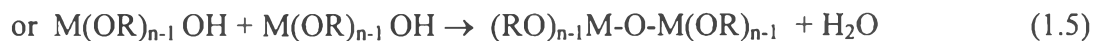
## 1.2 Sol-Gel Process

The sol-gel process is a versatile solution process for making ceramic and glass materials; it is a modern synthesis technique for special ceramics. It generally refers to the transition of a system from a liquid phase (sol) into a solid phase (gel), and more importantly produces better purity and high homogeneity at low temperature.

The sol-gel process involves a preparation of the sol from metal-organic compounds, such as metal alkoxide $M(OR)_n$, a precursor that is soluble in many solvent. In a typical sol-gel process, the precursors are subjected to a series of hydrolysis and condensation reactions: For example, metal alkoxide $M(OR)_n$ as a precursor involves two important reactions:

1.  Hydrolysis;

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}OH + ROH \quad (1.3)$$

2. Condensation;

$$M(OR)_n + M(OR)_{n-1} OH \rightarrow (RO)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + ROH \qquad (1.4)$$

$$\text{or } M(OR)_{n-1} OH + M(OR)_{n-1} OH \rightarrow (RO)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + H_2O \qquad (1.5)$$

The hydrolysis reaction is first initiated, followed by the condensation reactions (1.4) or/and (1.5) to give the metal–oxygen–metal (M-O-M) bond, and eventually a network or gel. In either case, the conversion of the molecular solution into a gel is achieved by using water. Hereby, the alkoxide molecules are hydrolyzed and have undergone condensation reaction to form a macromolecular network of wet gel. The gel is then dried and slowly solidified while the remaining water and traces of organic material coming from alcohol generated inside the pores of the dried gel are removed by calcination.

The factors affecting hydrolysis and condensation reactions to from gel are:
   a) Electronegativity of the metal atom to increase the coordinate number.
   b) Steric hindrance of the alkoxy group (-MOR).
   c) Molecular structure of the metal alkoxides (monomeric or oligomeric)
   d) Amount of added water in thy hydrolysis step and sequence of water addition.
   e) pH.

When applied to a multinary system like lead zirconate titanate, this principal synthesis technique needs to be extended and modified. The choice of the starting materials is dictated by a number of factors including reactivity, solubility, organic content, decomposition temperature, product costs and availability.

## 1.3 Objectives

The objectives of this thesis work are to prepare PZT directly from moisture stable and easily synthesized zirconium, titanium and lead glycolate via the sol-gel process with and without the microwave technique, and to characterize the PZT

product using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Thermogravimetric Analyzer (TGA), Fourier Transform Infrared (FTIR) spectrometer to follow the sol-to-gel transformation and SEM-EDS to determine the morphotropic phase boundary (MPB) of the Zr/Ti ratio.