CHAPTER 2

LITERATURE REVIEW

This chapter is focused on the perovskite ferroelectrics in the lead magnesium niobate-lead titanate (PMN-PT) solid solution system. The necessary general background includes an outline of the perovskite ferroelectrics with more detailed description of the normal and relaxor ferroelectrics. The relevant literatures on preparation and characterization of PMN, PT and PMN-PT are reviewed with attention paid on their processing-structure-property relationships.

2.1 Perovskite Ferroelectrics

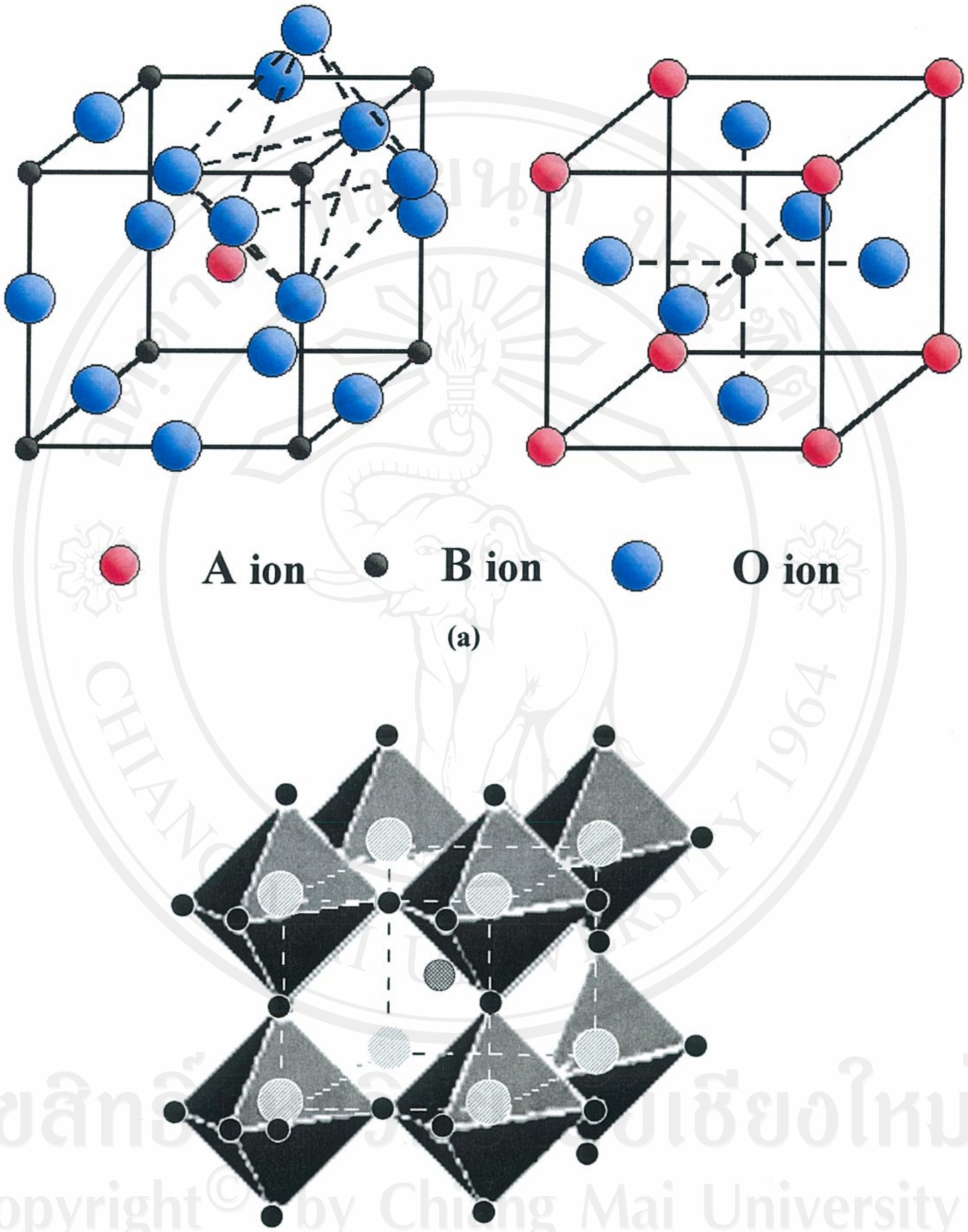
The largest group of ferroelectric and related materials are based on the simple perovskite structure, ABO_3. The first perovskite discovered to exhibit ferroelectricity was barium titanate, $BaTiO_3$, from which an extensive family of important isomorphs has been established. The perfect prototype perovskite is generally described as having simple cubic structure and takes its name from the isostructural mineral "perovskite" calcium titanate, $CaTiO_3$.[7]

In this simple cubic structure the A-site is occupied by large cations (Pb, Ca, Ba, Sr, Na, K) of 12-fold coordination which are located at the corners of the unit cell. The B-site is occupied by smaller highly-charged cations (Ti, Zr, Nb, Ta, W) of 6-fold coordination which are situated at the small octahedral site in the body center of the cell. The six-coordinated oxygen anions are located at the face centers of the cube. Examples of some simple ABO_3 perovskite compounds are $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, $NaNbO_3$ and $SrTiO_3$.[1,3]

For $BaTiO_3$, ABO_3, the larger A cation Ba^{2+} is located at the cube corners. The smaller B cation Ti^{4+} is located at the cube centre and is surrounded by an octahedral arrangement of the oxygen anions, positioned at the cube face centres. This particular representation of the structure is shown in Fig. 2.1(a). The perovskite structure can therefore be represented as linked framework of BO_6 (TiO_6) octahedra with the A-site ion in 12-fold co-ordination with oxygen and the B-site in 6-fold co-ordination, Fig. 2.1(b). In most cases the cubic structure in Fig. 2.1 is somewhat idealised.

As the temperature is lowered below the Curie point a displacive structural transformation of the prototype cell occurs and the formation of a spontaneous polarization accompanies the onset of ferroelectricity. In the case of the $BaTiO_3$ prototype cell structure, the lower symmetry pseudocubic distortions of tetragonal, orthorhombic and rhombohedral are observed with decreasing temperature. The simplistic two dimension potential-well model[2] has been commonly used to describe the onset of ferroelectricity and the reversibility of the polarization for $BaTiO_3$. Displacement of Ti^{4+} ion from the centre of oxygen octahedron, on transition from the paraelectric to tetragonal ferroelectric phase, is considered responsible for the spontaneous polarization.

The perovskite structure is tolerant of a very wide range of multiple cation substitutions on both the A-and B-sites. Of particular interest are complex lead-based perovskites having the general formula $Pb(B'_xB''_{1-x})O_3$, where B' is typically a low valence cation, e.g. Mg^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+}, In^{3+}, Sc^{3+}, and B''a high valence cation, e.g. Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}. In addition to many normal ferroelectric materials contained within this group, the complex lead-based perovskites also include a subgroup of materials characterized by a broad and strongly frequency dependent phase transition, the relaxor ferroelectrics. The major property differences which distinguish relaxor and normal ferroelectrics are summarized in Table 2.1.[1]



(a)

(b)

Fig. 2.1 (a) Perovskite ABO_3 prototype unit cell[8] and **(b)** linked framework of BO_6 octrahedra.[9]

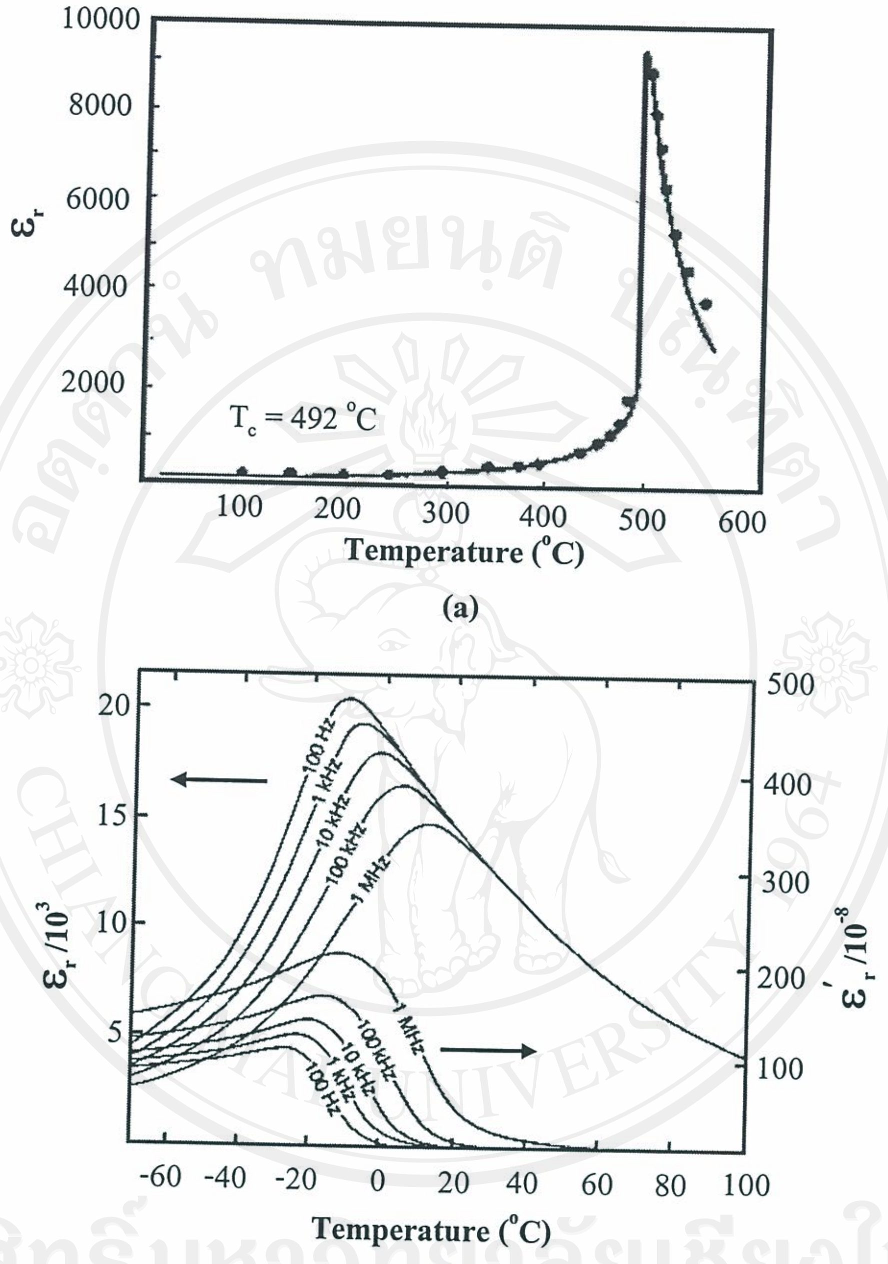
Table 2.1 Property differences between normal and relaxor perovskite ferroelectrics.[10]

Properties	Normal ferroelectrics	Relaxor ferroelectrics
Permittivity temperature dependence $\varepsilon = \varepsilon(T)$	Shrap 1st or 2nd order transition about the Curie temperature	Broad, diffuse phase transition about the Curie maximum
Permittivity temperature and frequency dependence $\varepsilon = \varepsilon(T, \omega)$	Weak frequency dependence	Strong frequency dependence
Remanent Polarization	Strong remanent polarization	Weak remanent polarization
Scattering of light	Strong anisotropy (birefringent)	Very weak anisotropy to light (pseodu-cubic)
Diffraction of X-rays	Line splitting owing to spontaneous deformation from paraelectric ⟶ ferroelectric phase	No X-ray line splitting, giving a pseodu-cubic structure

The nature of the polarization mechanism in these two groups are essentially the reason for large differences in behaviour. In normal ferroelectric there is long-range co-operative alignment of dipoles (or anti-dipole alignments) whereas in the relaxors there is only short-range ($\sim 100\,\mathring{A}$) co-operative alignment of dipoles forming thermally unstable polar micro-regions.[11,12]

In recent years research based on the class of ferroelectric ceramics known as relaxor has become widespread, both due to their potential in commercial applications and from scientific viewpoints.[1-6] Relaxors show several intriguing phenomena which clearly distinguish them from the normal ferroelectrics, Fig. 2.2 .[1] Instead of a sharp peak in the permittivity-temperature response (corresponding to a structural phase transition), they show a diffuse maximum in permittivity spreading over a wider temperature interval. The magnitude of maximum permittivity (or dielectric constant) can be markedly larger in relaxors than in normal ferroelectrics making them possible candidate materials where volumetric efficiency is paramount. The temperature coincident with the peak permittivity shows a strong frequency dependence, being shifted to higher temperatures as the measurement frequency is increased. The temperature at which the maximum in the dielectric loss occurs also displays frequency dispersion but in the opposite direction to that in the permittivity.

The diffuse permittivity-temperature behaviour of relaxors coupled with their desirable volumetric efficiencies has pushed much research in the direction of compositional design.[1,3,11] In this work, attempts have been made to synthesize the relaxor prototype of lead magnesium niobate (PMN) and its solid solution with normal ferroelectric lead titanate (PT) by employing a simple mixed oxide synthetic route.



(a)

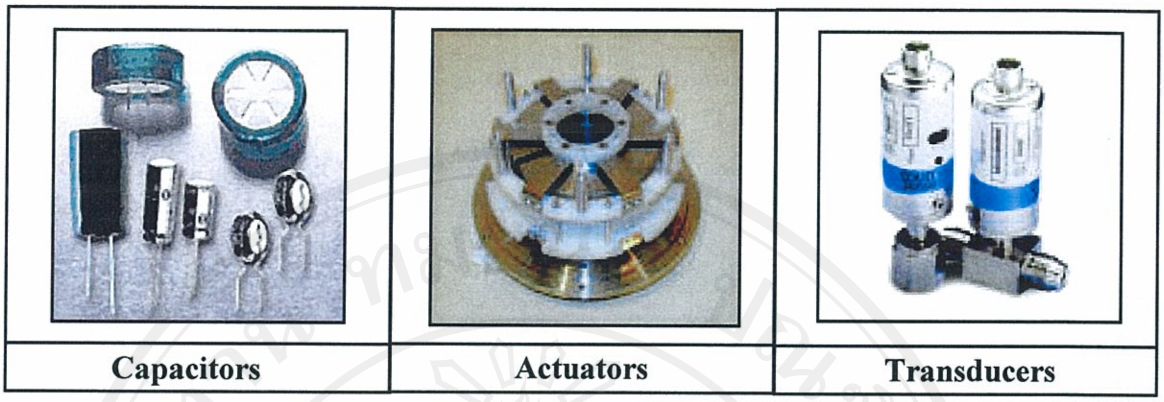
(b)

Fig. 2.2 (a) Normal[13] and (b) relaxor ferroelectric behaviours.[1]

2.2 Lead Magnesium Niobate (PMN)

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ or PMN, was first fabricated by Smolenskii and Agranovskaya[11] in the late 1950s and is one of the most studied of the complex lead-based perovskites. At room temperature, PMN exhibites a cubic perovskite structure with space group *Pm3m* and lattice constant $a = 4.04\,\mathring{A}$.[14] On cooling, this high temperature paraelectric phase undergoes a gradual transition into a rhombohedral ferroelectric state over a wide range of temperatures centered at approximately 0 °C. The origin of this broad dielectric response is postulated as caused by a distribution of Curie points resulting from microcompositional fluctuation in the B-site cations.[12]

PMN is a well-known relaxor ferroelectric whose excellent piezoelectric and dielectric properties ($\varepsilon_{r,max} \sim 20{,}000$ and $\tan\delta < 0.002$) along with its relatively low sintering temperature (1000-1250 °C) make it viable for use in a wide range of applications including multilayer capacitors, piezoelectric transducers, and electrostrictive actuators (Fig. 2.3).[1] However, the implementation of this material, and other relaxor compositions, for such commercial applications has been primarily hindered due to several processing-related factors. These include a lack of understanding and control over both the pyrochlore $\leftrightarrow$ perovskite phase transformation and lead volatility/loss during sintering. These factors result in poor reproducibility during fabrication and subsequent variations in dielectric behaviour. In recent years, however, significant progress has been made with regard to the development of improved processing schemes in an effort to control or eliminate these difficulties.



Capacitors | **Actuators** | **Transducers**

Fig. 2.3 Typically applications of PMN ceramics.[14,15,16]

2.2.1 Preparation of PMN powders

The difficulties encountered in the preparation of perovskite PMN powders have been well documented, particularly with respect to the issue of pyrochlore formation. This section describes the evolution of current PMN processing schemes, while providing information concerning reaction sequences and the parameters which affect them.

The preparation of pure lead-based relaxor ferroelectrics with the perovskite structure is very difficult by conventional ceramic processing techniques. Due to a preferential reaction between PbO and Nb_2O_5, the product obtained via single step mixed oxide reactions is nearly unavoidably a cubic pyrochlore of type $Pb_3Nb_4O_{13}$ or a rhombohedral pyrochlore of the type $Pb_2Nb_2O_7$, both of which are greatly detrimental to dielectric and piezoelectric properties.[17-20]

The problem of pyrochlore formation in PMN ceramics has been studied extensively. A reaction sequence for the formation of perovskite PMN was first proposed by Inada.[18] From extensive DTA and X-ray diffraction studies, he demonstrated that conventional mixed oxide processing formed both the cubic and rhombohedral pyrochlores before perovskite PMN was produced. He emphasized that the kinetics for the conversion of the pyrochlore phases to perovskite are very slow, and that to obtain single-phase perovskite PMN, it is necessary to prevent evaporation of PbO, which would slow down these reactions, and to use repeated grindings and calcinations.

The initial work of Lejeune and Boilot[19] considerd the many parameters which influence the synthesis of PMN from PbO, MgO and Nb_2O_5 precursors, concluding that the formation of a lead niobate pyrochlore phase could not be completely eliminated. Moreover, it was proposed that the reactivity of MgO with PbO and Nb_2O_5 was the definitive factor governing products of the reaction. These authors later proposed two modifications, i.e. the use of $MgCO_3$ in place of MgO, and milling in acetone instead of water.[21] These were found to increase the yield of perovskite PMN.

Swartz and Shrout[20] also studied the reaction kinetics of the formation of perovskite PMN from mixed oxides. They performed a calcination study and determined that: (1) higher calcining temperatures gave higher yields of perovskite phase, but even very high temperatures (950-1000 °C) still left considerable amounts of pyrochlore, (2) calcining longer than 4 h did not appreciably improve perovskite yields, and (3) excess MgO and PbO were always detected, thus indicating incomplete reaction. They concluded that the cubic pyrochlore ($Pb_3Nb_4O_{13}$) was very stable, and that Mg was able to be incorporated into the cubic pyrochlore structure as $Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}$. They also concluded that PMN formation is accelerated by PbO and MgO additions, thus the reactivity of MgO (and PbO to a lesser extent) are important factors to consider.

As a results, Swartz and Shrout[20] performed another calcination study concerned with the addition of excess MgO to compensate for poor dispersability and reactivity. They also did experiments to affect the volatility of PbO. As they surmised, excess MgO was found to increase the amount of perovskite PMN, as was increasing the calcining temperature; however neither succeeded at eliminating pyrochlore content completely. Also, they found that processes that reduced PbO less (such as short sintering times or closed crucible firing) increased the percentage of perovskite phase. Conversely however, processes leading to PbO loss increased pyrochlore content due to the reverse reaction.

Swartz and Shrout[20] finally concluded that even though the cubic pyrochlore phase could be eliminated by using excess PbO and MgO, repeated calcination would still have to be used, and the resultant PMN perovskite phase would be non-stoichiometric, thus having detrimental effects on dielectric properties.

To obtain stoichiometric phase-pure perovskite PMN, Swartz and Shrout[20] realized the need to eliminate the pyrochlore phase completely. Thus they pre-reacted the B-site cation oxides (MgO and Nb_2O_5) to form columbite $MgNb_2O_6$ via reaction:

$$1000\ ^{\circ}\mathrm{C} \qquad MgO + Nb_2O_5 \rightarrow MgNb_2O_6 \qquad (2.1)$$

Then they reacted the columbite with PbO after intense milling via:

$$700\text{-}900\ ^{\circ}\mathrm{C} \qquad MgNb_2O_6 + PbO \rightarrow 3Pb(Mg_{1/3}Nb_{2/3})O_3 \qquad (2.2)$$

This reaction sequence bypasses pyrochlore formation which results from the preferential reaction between PbO and Nb_2O_5. The product obtained with a single 4 h calcination at 800 °C was perovskite PMN with $<$ 5 wt% pyrochlore, as shown in Fig. 2.4.

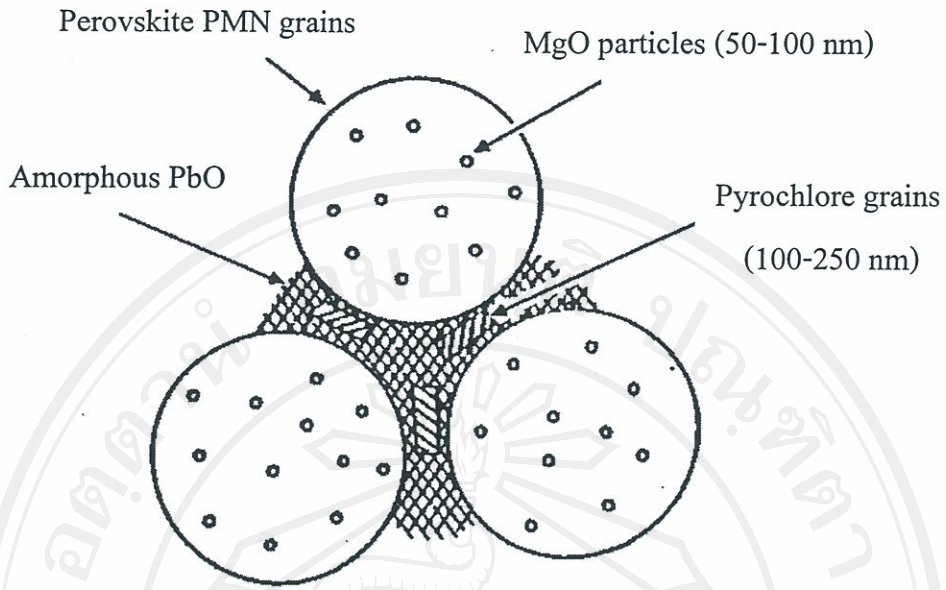


Fig. 2.4 Schematic illustration of the PMN microstructure.[20]

Butcher and Daglish[22] subsequently combined the approach of Lejeune and Biolot with that of Swartz and Shrout by investigating a two-stage synthesis with hydrated magnesium carbonate-magnesium hydroxide, $(MgCO_3)_4.Mg(OH)_2.5H_2O$ as a precursor. The essentially pyrochlore-free powders obtained could be attributed to its high reactivity with Nb_2O_5. Recent work[23] has confirmed the superiority of the two-stage synthesis, also highlighting the importance of the firing conditions in determining the yield of perovskite product.

In an attempt to avoid pyrochlore phase formation as well as to produce PMN powders of controlled morphologies, high purity and narrow size distribution, wet-chemical synthesis has evolved as a major field of research in recent years. The advantages of chemistry-based processing routes are obvious; they increase the homogeneity of resulting powders by mixing the reagents at the molecular level in solution. Techniques such as co-precipitation,[24] sol-gel,[25] citrate route,[26] molten salt[27] and partial oxalate methods[28] are among those which have been developed for the preparation of PMN powders. However, the success of precipitation or co-precipitation of solutes from a homogeneous solution is controlled by parameters such as solution pH, temperature, type and concentration of precipitant, hydrolysis rate of cations, ect.[29] The stoichiometry of a multicomponent compound may be lost when the precipitates involved exhibit very different solubility in the aqueous solution. Moreover, calcination temperatures in excess of 900 °C and addition of excess MgO are required to form phase-pure PMN. The current problems in sol-gel for oxide synthesis are related to phase separation during gel formation and/or gel thermolysis.[30]

2.2.2 Preparation of PMN ceramics

With the development of improved processing schemes capable of forming nearly phase pure perovskite PMN powders came an expanding interest in the sintering of powder compacts to high density and resultant dielectric properties. It should be noted that the dielectric properties and processing characteristics of ABO_3 perovskites are closely related to the cation stoichiometry or A/B ratio. Hence, for reliability and reproducibility, precise control of cation content is of utmost importance. When one of the cations is volatile under conditions of either powder synthesis or subsequent sintering, control of cation stoichiometry becomes nearly impossible. This is particularly true for Pb-based perovskites, most of which need to be sintered at temperatures greater than 900 °C. This temperature is high enough that substantial PbO loss occurs. For example, at 900 °C PMN loses about 0.5 wt%/h or 2×10^{-5} moles PbO/h.[25] This is high enough that PbO content becomes rather ill defined, especially when sintering at more commonly used temperatures like 1200 °C. Consequently, property reproducibility becomes a problem due to varying effects of low permittivity phase such as pyrochlore and amorphous PbO, which will be discussed later. As a result, initial firing studies were concerned with affecting sintering parameters in such a way as to limit PbO loss.

Lower sintering temperatures and shorter dwell times were found to increase perovskite yields, but at the expense of adequate densification and superior dielectric properties.[19] Limited PbO loss and, hence, minimal pyrochlore formation can be achieved, in addition to sufficient densification, by careful atmospheric control. This is generally accomplished through the addition of excess PbO to the calcined powders[21,31] or by use of a PbO source powder, e.g. $PbZrO_3$ or PMN, to provide a PbO-rich compensating atmosphere during sintering.[32-36] It should be noted also that excess PbO, if not thoroughly driven off through volatilization, can lead to reductions in dielectric constant, mechanical weakness, and aging.[37]

Even with painstaking care to eliminate pyrochlore formation via B-site precursor reaction and atmospheric control, however, one still encounters a great deal of variation and non-reproducibility in the dielectric properties of sintered PMN. The reasons for this are not clearly understood, although it is obvious to study the volume and connectivity of low dielectric constant phase(s) in these materials. These may include any or all of the following:

(1) isolated pyrochlore grains formed during powder synthesis,
(2) unreacted MgO present from incomplete precursor reaction,
(3) pyrochlore formed by loss of PbO from perovskite grains during sintering,
(4) MgO or MgO-rich phase also formed by PbO loss during sintering, and
(5) PbO-rich amorphous grain boundary phase.

It is noteworthy that PbO volatility has a direct impact on the formation and/or connectivity of three of these possible low permittivity phases, namely (3), (4), and (5). This leads to a short discussion of work that has been done with regard to the microstructure of PMN ceramics.

As already discussed, fabrication procedures for near phase pure PMN ceramics encompass a wide range of powder preparation and sintering variables, including excess MgO and/or PbO additions, atmospheric controls via PbO source powders, and various temperature/time heating profiles. Additionally, although the final product is often referred to as phase pure (within the limits of X-ray diffraction) perovskite PMN, extreme variations in reported properties, particularly values of maximum permittivity, exist. As a result, a significant amount of work has been done upon the microstructural characteristics of this material in an effort to better understand these processing-property relationships.

A grain size dependence of dielectric constant in PMN ceramics was first reported in 1984.[32] In this study additions of excess MgO and higher sintering temperatures were both found to increase the average grain size, resulting in corresponding increases in dielectric constant. They proposed that this implied grain size dependence was actually caused by the influence of a volume of low permittivity phase distributed within the grain boundaries. From microstructural analyses in which they noted the presence of mechanically weak grain boundary phase and a lack of MgO or pyrochlore in the perovskite grains, it was postulated that MgO and/or pyrochlore were/was present in some form of grain boundary phase.

Transmission electron microscopy (TEM) work by Goo *et al.*[38] identified the grain boundary phase as an amorphous PbO matrix within which existed well-faceted, submicron pyrochlore crystals. Contrary to Swartz *et al.*[32], they located submicron MgO inclusions within the perovskite PMN grains, although it was not indicated whether they precipitated there or were engulfed by grain growth. A schematic illustration of this microstructure can be seen in Fig. 2.4. Additionally, it was suggested that excess PbO could decrease sintering temperatures due to liquid phase formation, and thus be used as a densification aid. However, they disputed the claims of Lejeune and Boilot[39] that excess PbO would reduce pyrochlore content.

Chen *et al.*[33] observed large discrete grains of pyrochlore within the structure and by analysis suggested that such an isolated low-ε_r phase would not significantly dilute the magnitude of dielectric constant of ceramic. Hence they looked at simple modelling of dielectric constant as a function of grain boundary thickness, which demonstrated the potentially strong influence of low-ε_r intergranular phases upon the overall dielectric constant. Shrout *et al.*[34] noting that samples with higher weight loss due to PbO volatility had generally higher dielectric constants, believed this influence of low-ε_r PbO-rich grain boundary phase would explain the observed grain size dependence of dielectric constant found in their study.

Finally, Wang and Schulze[36] noted the presence of MgO as both micron-sized spherical particles within the grain boundaries and as discrete particle inclusions within the PMN grains. They also observed a decrease in the dielectric constant with additions of excess PbO. This was explained by a "grain boundary thickening" effect. Modelling of dielectric constant as a function of grain boundary thickness suggested that stoichiometric PMN had an amorphous PbO-rich grain boundary of thickness 10-50 $\mathring{A}$, which became thicker with excess PbO additions.

In summary, microstructural characterizations of PMN have proven to be extremely valuable in terms of examining processing variables such as excess PbO, excess MgO, and pyrochlore content, and in determining their effects upon certain properties, i.e. modelling dielectric constant as a function of pyrochlore content or grain boundary thickness.

2.3 Lead Titanate (PT)

Lead titanate ($PbTiO_3$ or PT) is a ferroelectric with a high Curie point (~ 490 °C) at which the phase transition from the cubic paraelectric (above Curie point) to the tetragonal ferroelectric phase (below Curie point) occurs.[13] At room temperature, PT has a symmetry of point group *4mm* with the ratio of axes $c/a \sim 1.063$, which is larger than that ($c/a \sim 1.01$) for barium titanate.[1,2] It is very appropriate for high frequency and high temperature applications in electronics and microelectronics, due to its desirable dielectric constant ($\varepsilon_r \sim 200$), pyroelectric, and piezoelectric

($k_t/k_p > 10$) properties.[1,3,13] It has been extensively employed to make solid solutions with lead zirconate ($PbZrO_3$) to obtain lead zirconate titanate (PZT) material[3] and also other perovskites, forming a wide range of versatile crystalline solid solutions, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$- $PbTiO_3$ or PMN-PT and $Pb(Zn_{1/3}Nb_{2/3})O_3$- $PbTiO_3$ or PZN-PT.[1,3] These PT-based family members of ferroelectrics are widely used in multilayer capacitors, actuators, sensors, transducers, pyroelectric detectors and electro-optic devices (see also Fig. 2.5).[1,3]

In all these applications, if the processing temperatures are maintained higher than the PbO melting temperature (~ 880 °C), the performance of these devices is affected due to PbO volatilisation. Therefore, to avoid PbO loss, the focus of current research activities over the past few decades is to synthesize stoichiometric $PbTiO_3$ powders at lower temperatures having controlled physical and chemical characteristics.[40-43] Many investigations have thus focused on the processing of PT powders via several preparation routes, such as mixed oxide,[40] sol-gel,[41] co-precipitation,[42] hydrothermal reaction[43], to name a few of the many. However, the degree of success of these techniques in preparing PT powder varies considerably from one to another.

Fig. 2.5 Variety of ferroelectric PT-based ceramics used in electronic applications.[3]

2.3.1 Preparation of PT powders

The stoichiometry of $PbTiO_3$ is known to be an important factor for ensuring good electrical characteristics.[1,3] Generally, the conventional method adopted for its preparation involves the heating of mixture of lead oxide and titanium oxide above 1000 °C,[44] a temperature significantly above the melting point of PbO, which usually leads to Pb-deficient $PbTiO_3$.[45] The phase equilibria in $PbO\text{-}TiO_2$ system is shown in Fig. 2.6. It is seen that $PbTiO_3$ forms from solid-state reaction of PbO and TiO_2 as low as 360-375 °C and has two eutectics.[13]

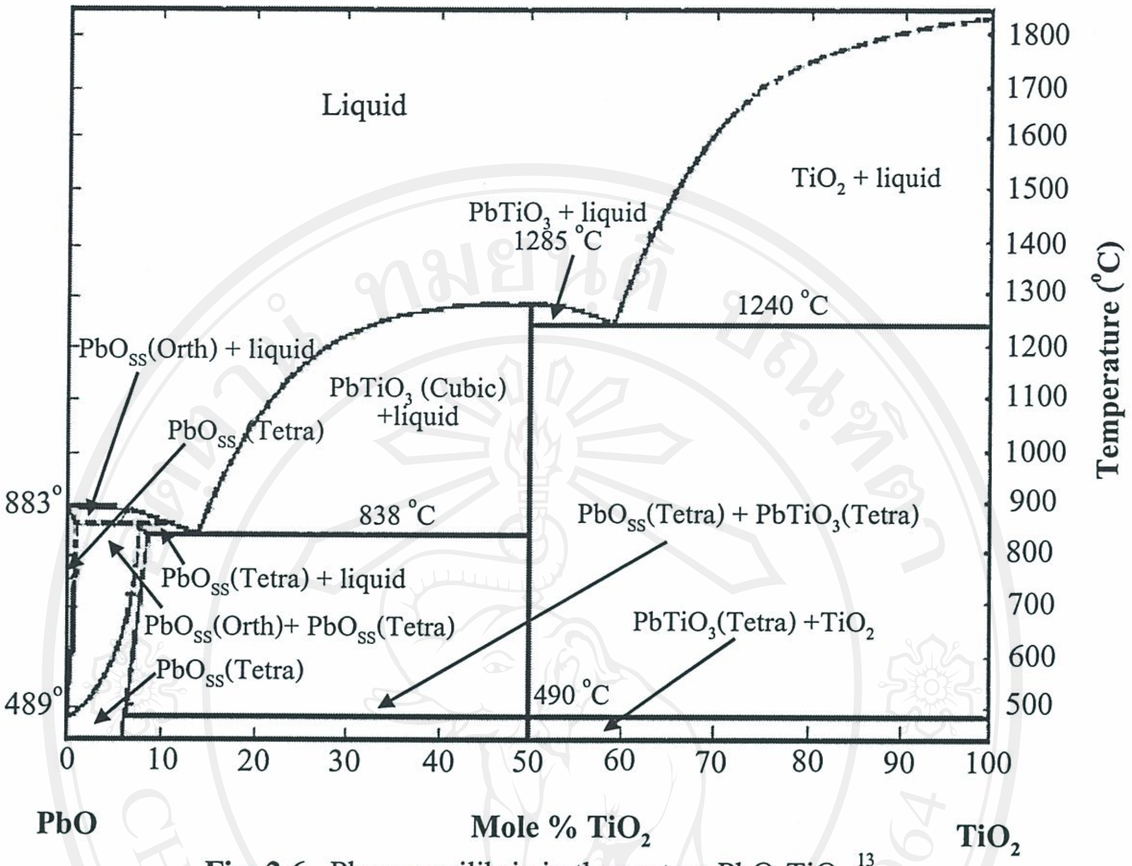


Fig. 2.6 Phase equilibria in the system PbO-TiO_2.[13]

In 1996, Pillai and Ravindran[40] have undertaken a systematic study of the reaction between PbO and TiO_2 using DTA and XRD techniques (Figs. 2.7 and 2.8). They reported that single-phase perovskite PT can be prepared by a conventional solid-state approach at a temperature as low as ~ 600 °C. However, the optimisation of calcination conditions used in mixed oxide process have not received detailed attention, and the effect of applied dwell time and heating/cooling rates have not yet been studied extensively. Much of the work concerning the $PbTiO_3$ compound has been directed towards determining sintering behaviour[46] and electrical properties.[47] Only limited attempts have been made to improve the yield of PT optimising processing steps.

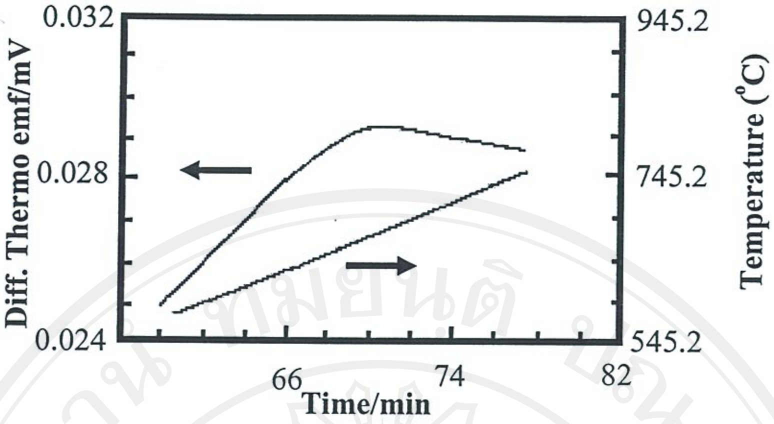


Fig. 2.7 DTA curve for the formation of lead titanate at a heating rate of 10 °C/min.[40]

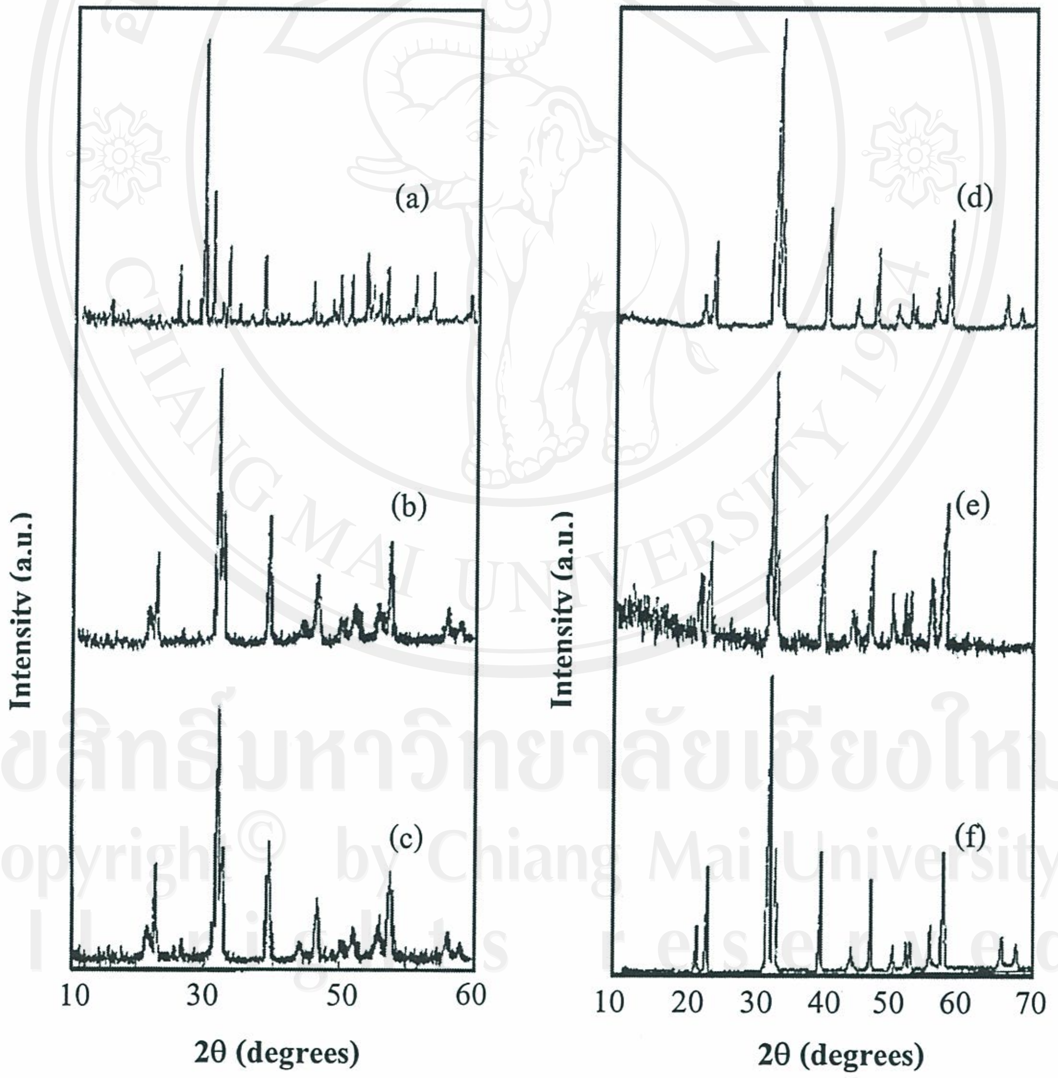


Fig. 2.8 X-ray diffraction patterns for the mixtures of PbO and TiO_2 in various heated treatment at : (a) uncalcined, (b) 527 °C for 26 h, (c) 577 °C for 7 h, (d) 602 °C for 2 h, (e) 1002 °C for 1.5 h, and (f) 1002 °C for 1.5 h after reheated to 602 °C for 2 h.[40]

More recent attempts to fabricate phase pure PT powders have come in the areas of wet-chemical and mechanochemical methods. Among the wet-chemical methods, co-precipitation is a simple and convenient method of achieving the chemical homogeneity through intimate contact and mixing of constituent ions on molecular level under controlled conditions.[48] Fang *et al.*[42] reported that the formation temperature for a single tetragonal PT phase via the co-precipitation route is as low as 500 °C (Fig. 2.9(a)), which is lower than those reported for most chemistry-based routes such as sol-gel technique (Fig. 2.9(b)).[41] However, the method did not give reproducible powders due to a thermodynamical preference for precipitation of lead oxalate and titanium hydroxide separately.[42]

The sol-gel route is well suited to the preparation of powders and thin films of PT.[49-51] This process involves the preparation of polymerizable solution, which is diluted and partially hydrolyzed. A polymeric gel is formed and the resulting dried amorphous bulk is further heat-treated to remove the organic residues and obtain the crystalline phases. Sol-gel derived PT powders have been reported to crystalline directly into the perovskite structure, while thin films often form first in the cubic paraelectric pyrochlore phase[49,50] and subsequently transform to perovskite at higher (500-700 °C) temperatures. Calzada *et al.*[48] reported that the formation of pyrochlore, a metastable intermediate phase, and/or lead-deficient secondary phases, $PbTi_3O_7$, delay the formation of perovskite phase and can damage significantly the electrical properties. Several researchers have synthesized crystalline PT in a two-step processes, i.e. by homogeneously precipitating a precursor salt at low temperatures and calcining it to form $PbTiO_3$ at higher temperatures. Fox *et al.*[52] precipitate an amorphous precursor powder at ~ 50 °C using $Pb(NO_3)_2$ and $TiCl_4$ with the addition of $NH_{3(aq)}$ and H_2O_2. The powder was calcined at 600 °C. Greninger *et al.*[53] reported a similar synthesis using $TiCl_4$, $Pb(NO_3)_2$ or $PbCl_2$, H_2O_2 and $NH_{3(aq)}$ as reagents, a precipitation temperature of ~ 20 °C, and a subsequent calcination at 800-1000 °C. However, the powders produced from these processes usually suffer from severge agglomeration, a broad particle size distribution, and poorly defined particle shape (Fig. 2.10).

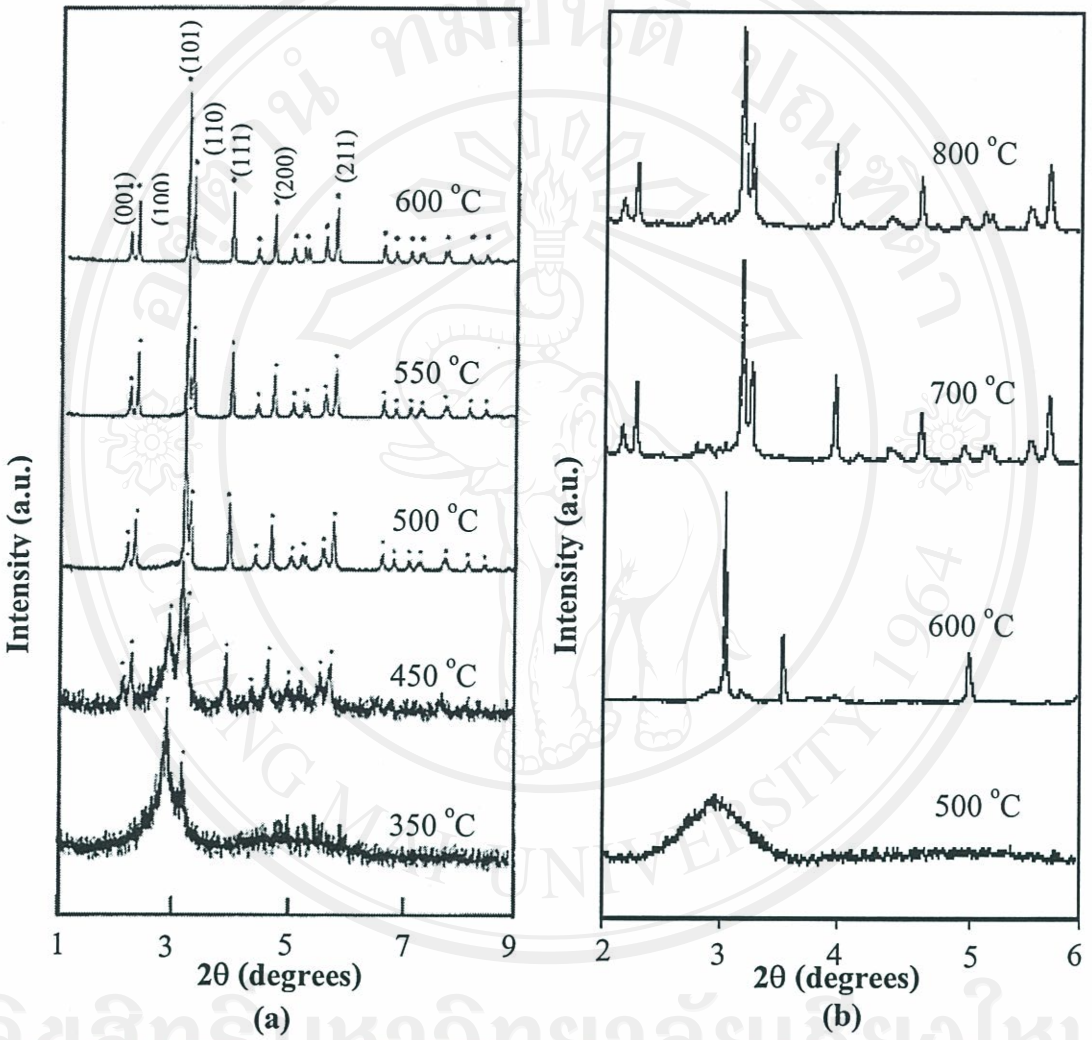
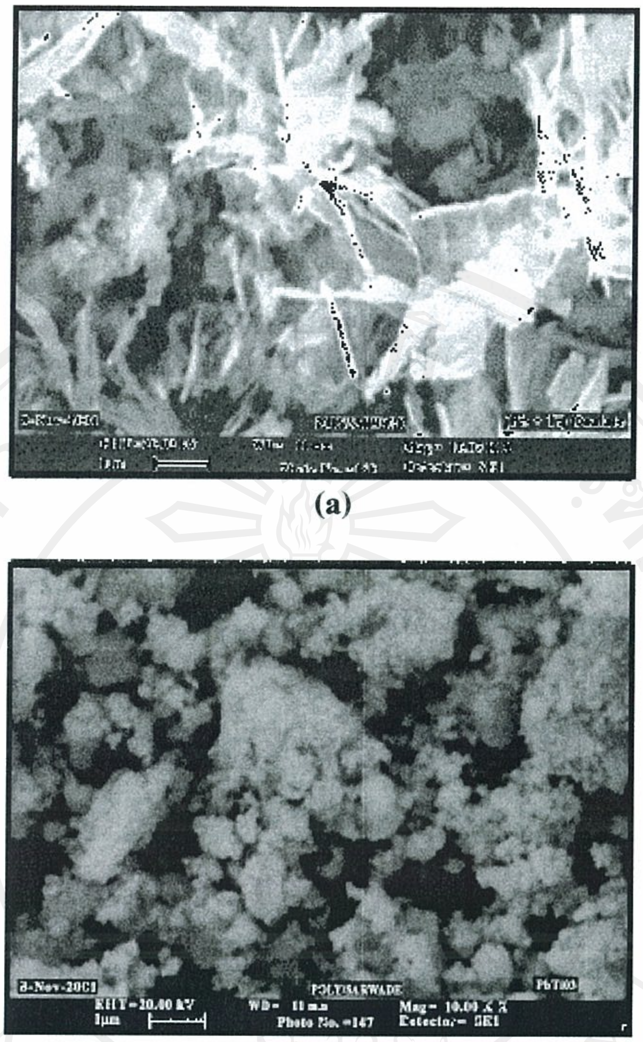


Fig. 2.9 (a) XRD traces of the $PbTiO_3$ powders prepared via the coprecipitation route and calcined for 1 h at 350, 450, 500, 550 and 600 °C, respectively and (b) X-ray diffraction pattern for heat-treated PT powder, strating from the powdered dried gel.[41-42]



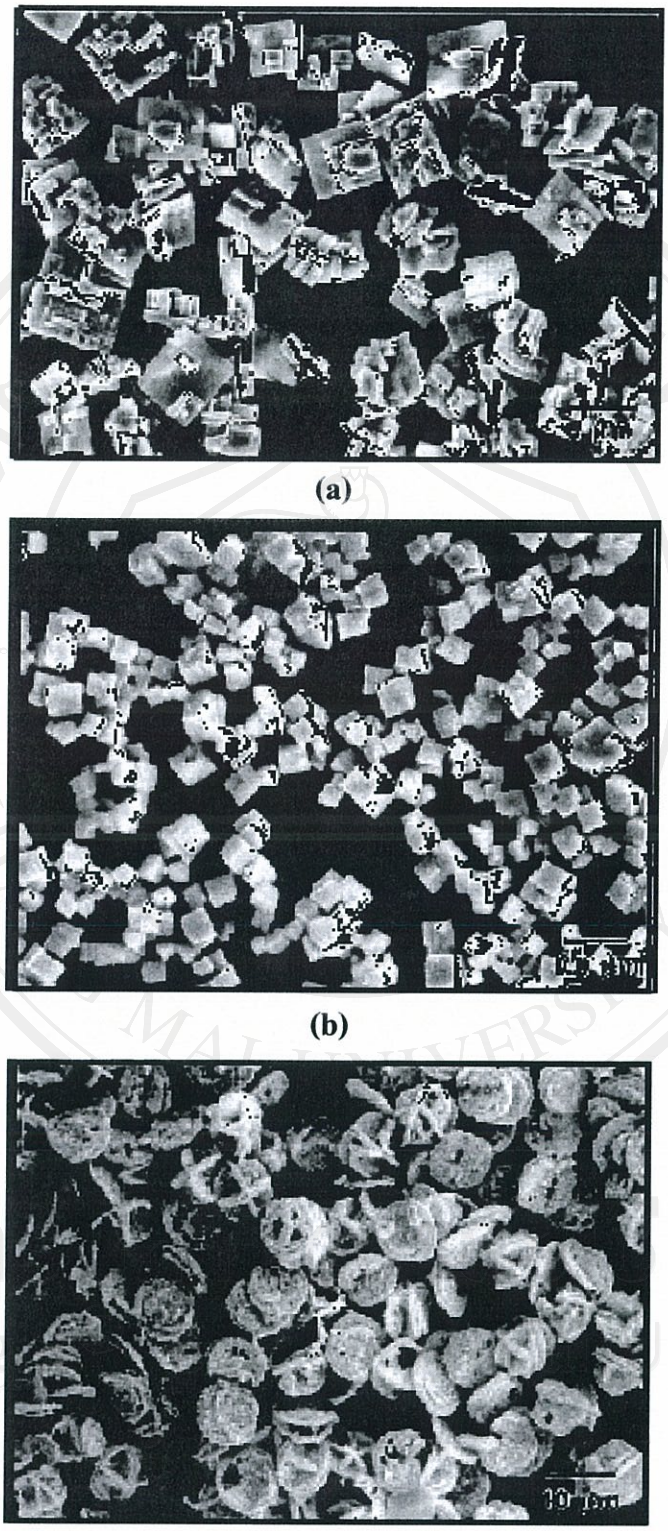
(a)

(b)

Fig. 2.10 SEM micrographs of (a) as dried mixed (Pb+Ti) oxalates precursor and (b) mixed (Pb+Ti) calcined at 750 °C/4 h.[52]

Hydrothermal synthesis of PT powders has several advantages over co-precipitation and sol-gel methods. Lead titanate particles with various morphologies (Fig. 2.11 (a-c))[54] have been prepared by this technique. Recently, nearly monodisperse cubic PT has been synthesized at temperature as low as 150 °C using the modified titanium isopropoxide precursor.[55] Sato *et al.*[56] synthesizes perovskite PT in a highly alkaline condition at 170 °C. The resulting products were agglomerated cubelike particles. Cheng *et al.* [57] have synthesized acicular PT particles with a tetragonal body-centered structure using hydrothermal conditions and lead nitrate and titanium butoxide. Ohara *et al.*[58]demonstrated that fibrous PT can be directly produced at 150 °C reacted for 72 h.

Fine PT precursor powders such as hydroxides and oxalates of high chemical homogeneity and purity can be realized, in principle, by adjusting the various processing parameters involved in each of chemical routes. However, almost all these wet-chemistry routes require the precursors be calcined at a temperature in the range of 500 to 800 °C, in order to develop the designed PT phase. This leads to the occurrence of the particle coarsening and aggregation and therefore ruins almost everything offered by the deliberately designed chemical routes, such as high specific surface area and refined particle size. The presence of hard particle agglomerates will significantly lower the sinterability of the resulting powder.



(a)

(b)

(c)

Fig. 2.11 SEM micrographs of $PbTiO_3$ synthesized at different concentration conditions of (a) 0.05 M (b) 0.1 M and (c) 0.125 M.[54]

More recently, mechanochemical synthetic route was developed has been applied to prepare a few ferroelectric powders, although in many cases it was not very successful.[59,60] The chemical reactivity of starting materials could be improved significantly upon an appropriate mechanochemical treatment, and the subsequent calcination temperature for forming the designed phase was lowered. Xue *et al.* [61] have demonstrated that perovskite PT powder can be synthesized directly by a mechanochemical method without being subjected to calcination. However, an activation time of at least 5 h are required to trigger the formation of PT phase.

In general, the overriding aim of any materials processing technique is to achieve a final product with consistent properties. In practice, the level of consistency obtained is often a matter of compromise, it being largely a consequence of the economics of fabrication and characterization. The mixed oxide synthetic route is probably one of the most fundamental, practical routine methods which has been used, and it has been developed and modified in both scientific research and industrial mass production for many years. This technique involves powder mixing, milling, drying, sieving and calcination. The effects of calcination parameters in process such as firing temperature on the powder characteristics have been widely studied. However, studies about the effects of dwell time and heating/cooling rates on the phase formation and morphology development are seldom reported. Whereas purity and reactivity are crucial, attention should also be given to the processing-property relationships of the final product, with a view to enhancing overall understanding.

2.3.2 Preparation of PT ceramics

It is well known that preparation of pure, dense $PbTiO_3$ ceramics via conventional sintering processes is difficult and it is widely regarded to be one of the most difficult lead-based ferroelectric materials to fabricate.[44] This is mainly due to the anisotropic thermal expansion from the cubic paraelectric phase to the tetragonal ferroelectric phase (with significant anisotropy of the tetragonal unit cell, where *c/a* ratio ~ 1.065) during cooling from high sintering temperatures.[62] The phase transition creates large internal stresses, resulting in fragility and finally destroys ceramics with numerous microcracks. Moreover, pure PT ceramics also exhibit low resistivity (10^7-10^8 Ω.cm at room temperature), which is a result of Pb vacancies created during the sintering.[63] Because a large lattice anisotropy exists, a very high electric field and high temperature are required for their poling.[64] However, it is impossible to apply such severe poling conditions to ceramics with low resistivity.

By substitution with small amounts of dopants, such as alkaline or rare earth elements, the lattice anisotropy is reduced, making it possible to produce dense ceramics with enhanced mechanical, dielectric and piezoelectric properties.[63-66] Other additives, such as Bi and Y, were also successfully used to improve the properties of PT ceramics.[67] Futhermore, addition of these ions lowers the sintering temperature and consequently suppresses lead volatilization. Substitution into the Ti^{4+} sites by Mn^{4+} enhances resistivity by compensating charges due to off-valence substitution for Pb^{2+}sites. As a result, modified $PbTiO_3$ ceramics can be subjected to severe poling conditions, and saturated piezoelectric properties can be obtained.[63]

Besides having a high Curie temperature and a low dielectric constant, modified $PbTiO_3$ ceramics posses large electromechanical anisotropy, along with large thickness and small planar coupling factors. These properties are useful for high-frequency applications such as ultrasonic transducers and SAW (Surface Acoustic Waves) devices, and low-frequency applications such as hydrophones.[63,68]

When modified PT ceramics are used as targets, dopant cations can be incorporated in the sputtered films, and they can alter the electrical and electronic properties compared with that of undoped PT films. Therefore, preparation of pure, dense PT ceramics is required, particularly relatively large-sized disks in excess of

7.62 cm in diameter, because this is the smallest substrate size used in the sputtering process.[69]

Spontaneous cracking in polycrystalline ceramics results from internal stress among the grains, which is caused by incompatible strains from thermal expansion anisotropy during the phase transformation. The area from which the microcracking is likely to begin is defined by a certain grain size limit.[70] Lead titanate has been reported to crack spontaneously when the average grain size is larger than ~ 3 μm and to completely disintegrate into powders when the grain are larger than 10 μm.[71] Therefore, one plausible way to fabricate pure PT ceramics with lower internal stress is to reduce the grain size (below 3 μm); the binding force between the grains may increase with the relative area of the grain boundaries.[72] However, dense ceramics with fine grains (< 3 μm) are difficult to prepare via conventional sintering processes.

Kim *et al.*[73] reported that they successfully fabricated crack-free, PT ceramics from sol-gel derived PT powders. Be carefully controlling the calcination temperature of the gels and the sintering parameters of the sol-gel derived powders, the grain sizes of the powders and the sintered PT ceramics were < 0.2 μm and 1.8 μm, respectively. Recently, Kong *et al.* [74] have applied a high-energy ball milling technique to the mixture of PbO and TiO_2 for 20 h and have obtained dense PT ceramics with submicrometer-sized grains (< 1.5 μm), as shown in Fig. 2.12.

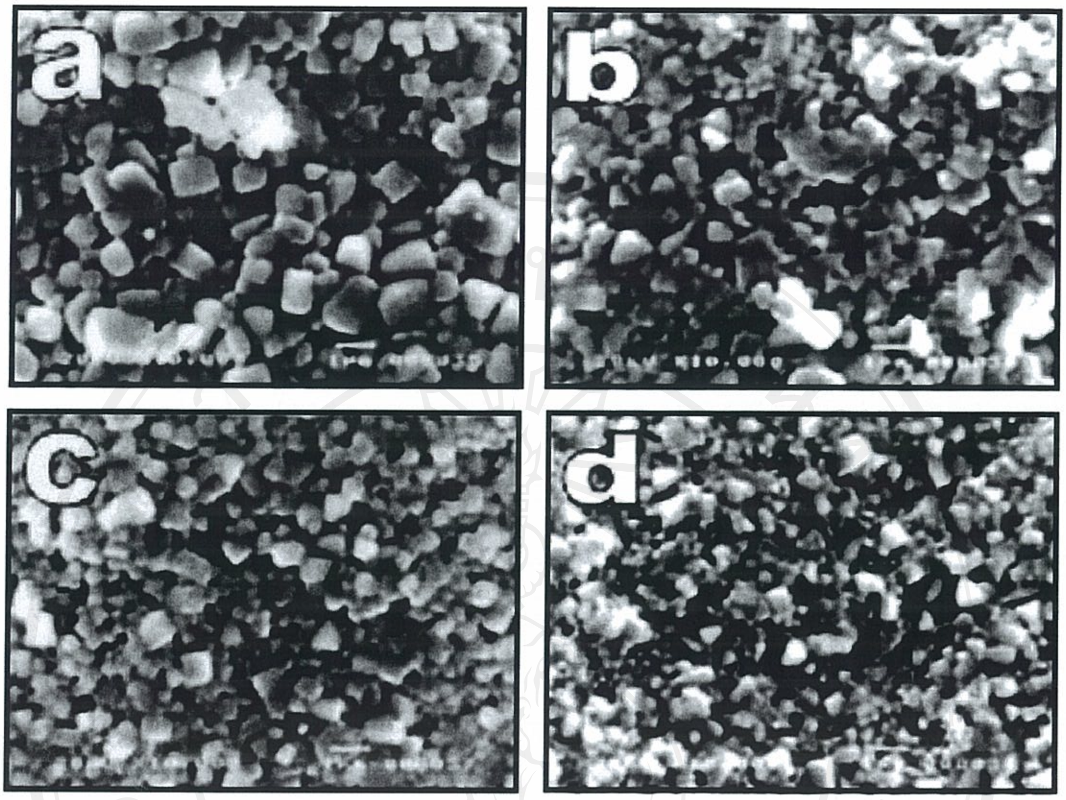


Fig. 2.12 The surface microstructure of the $PbTiO_3$ ceramics sintered at 1100 °C for (a) 20 h (b) 40 h (c) 60 h and (d) 80 h.[73]

Many attempts have been tried to build up the relationship between microstructure and properties of PT ceramics to improve mechanical properties as well as piezoelectric properties. Matsuo and Saski[72] reported that the poor mechanical strength originated from grain-grain separation due to different thermal coefficients in different crystallographic axes. They also made a point that heat treatment conditions had to be set up for each additive as showing that MnO_2 doped ceramics sintered at 1130 °C was mechanically strong but was fragile when sintered at 1150 °C. Ishikawa *et al.*[75] investigated the effect of particle size on the ferroelectric phase transition using PT particles derived from the alkoxide method. According to them, the phase transition shifts to higher temperature as the particle size increases up to 50 μm and then remain constant. This has been explained as the contribution of strong depolarization making the ferroelectric phase unstable, particularly in thin films.

Although the preparation of modified PT ceramics is relatively easy, rigorous control of the stoichiometry and homogeneous distribution of the dopants is necessary to avoid inhomogeneities in the microstructures of sintered bodies, which can result in microcracks, lower density and degraded electrical and mechanical properties especially at high temperature. Therefore, the fabrication of pure, dense PT ceramics is still required, particularly for electrical devices to be used at high frequency and high temperature.

2.4 Lead Magnesium Niobate-Lead Titanate (PMN-PT)

During several past decades, many experiment[76-78] studies were carried out on various phase transformation and crystal structures of lead-based perovskite-type solid solutions consisting of normal and relaxor ferroelectric materials. These compounds have attracted a growing fundamental and practical interest because of their excellent dielectric, piezoelectric and electrostiction properties which are useful in actuating and sensing applications.[2,4] Experimentally it has been reported that a variety of complex-mixed perovskite ferroelectrics with a complex occupation of the A and/or B site in the crystal lattice and exhibiting the diffuse phase transition behaviour have a nanometer scale heterogeneity in composition.[79,80] In the 1950s, Smolenski and coworkers[12,13] investigated many cation substitutions into $PbTiO_3$ in a search for a new ferroelectric materials. In this kind of substitution, the general guidelines are that the ionic sizes should be comparable to those of Ti^{4+} ion and the combination must yield the same average charge as Ti^{4+} to maintain charge neutrality. Many such compositions take on the complex perovskite structure, and their properties have been extensively reported by several researchers.[15, 81-83]

Lead magnesium niobate (PMN) is nowadays acknowledged as the representative of relaxor ferroelectrics.[11] The real macroscopic phase transition of the first order to rhombohedral long-range ferroelectric ordered phase has been detected in

PMN at about 200 K by cooling in an external dc electric field.[81] Though the Curie temperature or better yet, Curie range of PMN is well below room temperature, it can be easily shifted upward with PT additions, a normal or ordered ferroelectric compound which has a transition at 490 °C. A spontaneous (zero field) phase transition was indicated in the solid solution PMN-PT as a result of a change in the degree of ordering induced by substitution of cationic sites. An addition of ~28% PT causes the material to revert to a normal ferroelectric tetragonal phase with $T_C \sim 130$ °C.[82]

The (1-x)PMN-(x)PT system also show a morphotropic phase boundary (MPB) near $x \sim 0.4$, separating pseudo-cubic phase and tetragonal phases (Fig. 2.13).[82] As observed in other systems such as (1-x)PZN:(x)PT and (1-x)PZ:(x)PT or PZT, anomalously large dielectric and piezoelectric properties are observed for compositions lying near the MPB. The piezoelectric properties of PMN-PT system, however, are much higher compared with PZT system.

There is considerable interest in PMN-PT ceramics due to their high strains with low hysteresis losses. These compounds also exhibit a board maximum in the dielectric constant, and the temperature of the dielectric maximum also increases with the testing frequency as shown in Fig. 2.14. These properties make the materials particularly suitable for use in electrostrictive actuator, sensor and piezoelectric devices.

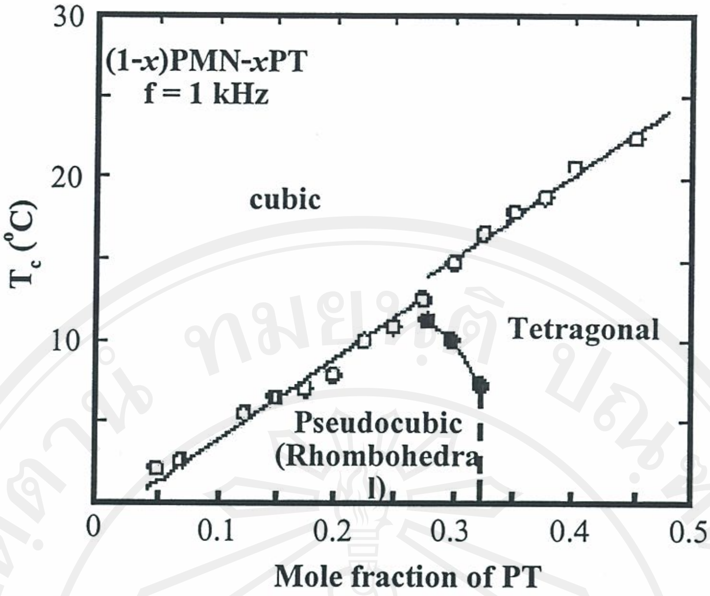


Fig. 2.13 Phase diagram of the PMN-PT solid solution system.[82]

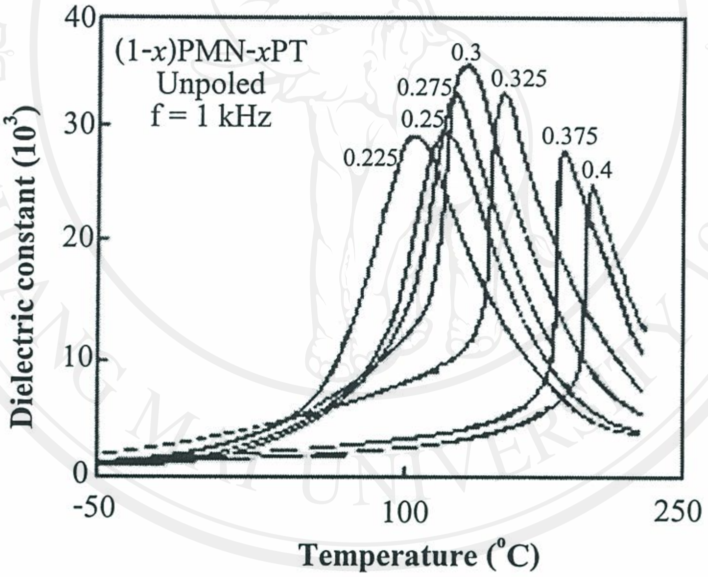


Fig. 2.14 Dielectric behaviour of (1-x)PMN-xPT ceramics at 1 kHz measuring frequency and as a function of temperature.[82]

There are several[83-91] reports on the properties of PMN-PT solid solution with various concentrations of PT. Recent publications have shown that the PT-based relaxors can offer improvements in high dielectric constants and electromechanical coupling. The most popular specific composition in this system is (0.9)PMN-(0.1)PT, which is PMN containing 10% PT, thus increasing the T_m (the temperature of maximum dielectric constant for relaxors, equivalent to T_c for normal ferroelectrics) of PMN to ~ 40 °C.[82] For this composition, the temperature of polarization loss (T_d) is ~ 10 °C ; hence, the material is a relaxor at room temperature (25 °C).

It is also an attractive replacement for $BaTiO_3$ in MLCs because it can be sintered at low temperature in comparison to $BaTiO_3$.[84,85] This powder has a vast promise for making polymer composite as a dielectric material in high performance capacitors. Takeuchi *et al.*[86] presented relaxor PMN-PT ultrasound transducers in which the properties of the transducer elements were switchable and tunable as a function of dc bias voltage. Their (0.9)PMN-(0.1)PT transducer elements exhibited an electromechanical coupling factor of approximately 0-0.40 with a dc bias field of 0-4 kV/cm. The operating frequency of the transducer elements could also be varied with the bias field, permittivity a true "tunable" ultrasound transducer. The ability to selectivity tune transducer elements and turn them on and off is attractive for many medical imaging applications.

Chen *et al.*[87] also investigated PMN-PT materials for medical ultrasonic transducer applications. Using a relatively low dc bias field of 5 kV/cm they achieved an electromehanical coupling factor of 0.43-0.50 and were able to measure a difference of approximately 30 dB in sensitivity when their test transducer was turned ON or OFF with a 5 kV/cm bias field. Their clinical imaging test results showed that a modified PMN-PT relaxor transducer can achieve performance as well as PZT, with the added potential for selectively controlling transducer elements.

The composition (0.93)PMN-(0.07)PT has been shown to have a large piezoelectric effect under electrical field.[88] Whereas, the composition (0.65)PMN-(0.35)PT has been shown to exhibit the highest piezoelectric properties. These compositions, as well as others in this solid solution system appear to be promising candidates for smart ferroic systems such as vibration control, actuator and sensor applications.[89,90]

In 1989, Choi *et al.*[83] investigated the dielectric and pyroelectric properties of relaxor ferroelectric (1-x)PMN: (x)PT solid solution series and observed an important contribution to the dielectric and pyroelectric response for the solid solutions compositions close to the morphotropic phase boundary ($x \sim 0.4$) between pseudocubic and tetragonal regions existing in the grains of the ceramic. Detailed characterization of these materials is given in Table 2.2. Moreover, anomalous dielectric and pyroelectric behaviour for compositions $x \sim 0.275$-0.35 mol% PT in the vicinity of morphotropic phase boundary were also observed.

Recently Brown *et al.*[91] reported their study on the dielectric and piezoelectric properties of (1-x)PMN:(x)PT across a compositional range which includes the MPB ($0 \leq x \leq 0.5$). The composition (0.95)PMN-(0.05)PT has been shown to exhibit great promise for sensor and actuator applications. It has been found that the transition temperature of (0.95)PMN-(0.05)PT ceramics (~ 20 °C) is closest to room temperature and thus showed the highest room temperature dielectric constant, consistent with Choi *et al.*[83] and Kelly *et al.*[90] However, in order to improve the ability to synthesize and process the materials for the "best" transducer devices, a fundamental knowledge of the atomic level structure and behaviour of these PMN-PT materials is required. They[91] also suggested that further work on powder processing by various solid-state reactions including the mixed oxide, columbite, wolframite and also molten salt methods should have been undertaken.

Table 2.2 Dielectric and piezoelectric properties of (1-*x*) PMN: *x* PT.[83]

Sample	Unpoled						Poled					
PMN-PT	ε_r	tanδ	$\varepsilon_{r,max}$	T_C(°C)	$\tan\delta_{max}$	d_{33}	ε_r	tanδ	$\varepsilon_{r,max}$	T_C(°C)	$\tan\delta_{max}$	d_{33}
0.775-0.225	3533	0.032	29552	112	0.036	297	1695	0.022	28688	114	0.042	96
0.75-0.25	2778	0.031	30192	127	0.061	305	2435	0.018	28714	130	0.072	124
0.725-0.275	2873	0.035	33432	136	0.045	353	2091	0.030	31986	138	0.051	130
0.7-0.3	3782	0.034	36469	139	0.035	669	4936	0.027	33289	143	0.057	136
0.675-0.325	4170	0.029	33350	155	0.029	663	5260	0.018	30048	159	0.049	156
0.65-0.35	3190	0.013	30623	177	0.098	456	3119	0.006	29020	182	0.069	230
0.625-0.375	2434	0.015	28524	190	0.018	405	2781	0.011	28126	198	0.038	191
0.6-0.4	2097	0.016	27156	202	0.030	323	2371	0.010	25189	207	0.044	204

Structural studies of PMN as a function of PT content have been reported by Viehland *et al.*[92] They demonstrated the presence of polar nano-domains for PT contents less than 30 at%, tweedlike structure for PT contents between 30 and 35 at%, and normal micron-sized ferroelectric domains for PT contents greater than 35 at%. In addition, La-modification of PMN-PT was found to result in the evolution of polar nanodomains and relaxor characteristics from the tweedlike structures. Other studies by Chen *et al.*[93] and Randall *et al.*[94] have reported the presence of short-range ordered domains on the scale of 2 to 5 nm which were characterized by the presence of 1/2 [111] superlattice reflections. These ordered regions did not coarsen on heat treatment.[95]

Furthermore, Chen *et al.*[93] suggested that short range ordered regions in PMN had a local Mg/Nb ratio of 1:1, relative to the global ratio of 1:2. It was then proposed that this local charge imbalance resulted in the stabilization of short-range ordered domains. Evidence in support of this hypothesis was demonstrated by donor and acceptor modifications onto the A-site of PMN. It was concluded that the degree of ordering and the size of ordered domains can be enhanced and reduced by donor and acceptor modifications, respectively.

For high performance it is essential that the material be of the perovskite crystalline phase with little or no pyrochlore phase. In the processing of perovskite solid solutions in the lead-based relaxor system $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, formation of an unwanted pyrochlore phase has long been recognized as a major problem for widespread use of these materials as multilayer capacitors.[96-98] The presence of the pyrochlore phase in the sintered ceramics, even in small quantities, has been associated with inferior dielectric properties of the materials.[99-100] It is difficult to prepare single-phase perovskite (1-*x*)PMN-(*x*)PT via the conventional solid-state reaction method. Numerous attempts have been made so far to develop a processing technique in which the formation of undesirable pyrochlore phase is suppressed. Among these, the

Columbite processing technique,[101] in which prefabricated $MgNb_2O_6$ is reacted with an appropriate proportion of PbO, has been widely used in the synthesis of phase-pure perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$–based materials. During the last several years, numerous studies[99-100] have been reported in the literature in which the Columbite processing technique was modified by using different sets of reactants as precursor materials. A different solid state processing technique[101] in which prefabricated $Pb_3Nb_2O_8$ is reacted with an appropriated proportion of MgO to yield a phase-pure product has also been used in the synthesis of pyrochlore-free perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$.

Several methods such as co-precipitation, sol-gel, gel combustion, and a molten salt method have been developed to prepare pyrochlore-free (1-x)PMN-(x)PT.[102-105] Although these approaches have significantly enriched the means of preparing PMN, problems still remain. For example, the sol-gel process uses expensive and moisture sensitive metal alkoxides, especially niobium ethoxide, which limits its commercial applicability for mass powder synthesis. The KCl molten salt process[84], one of the non-conventional mixed oxide processes, give single phase PMN-PT. But removal of KCl is difficult from lattice. Recently, high-energy ball milling has been successfully applied to synthesize pyrochlore-free nano-sized (0.9)PMN-(0.1)PT and (0.65)PMN-(0.35)PT powders after milling for only 2 h (Fig. 2.15).[106]

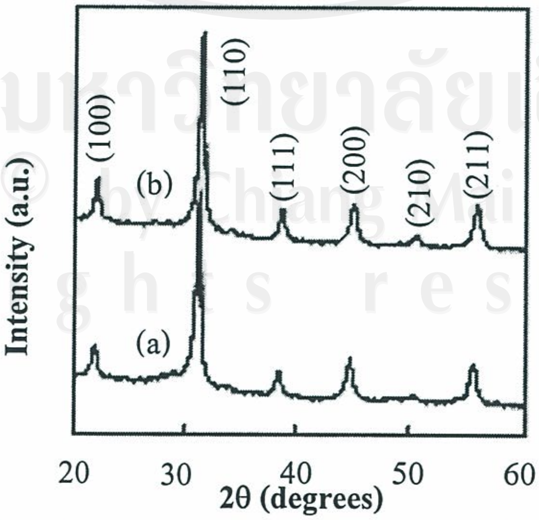


Fig. 2.15 XRD patterns for the mixed oxide mixtures: (a) 0.9PMN-0.1PT; (b) 0.65PMN-0.35PT milled for 2 h.[106]

Previous studies have been primarily concerned with processing characteristics and dielectric properties of the solid solution in which it has been demonstrated that both the starting materials and sintering conditions greatly influenced the densification process and dielectric properties of the resulting ceramics.

In addition to the above mentioned difficulties in the processing of phase-pure $Pb(Mg_{1/3}Nb_{2/3})O_3$-based perovskite solid solutions, another area of concern, which has an important bearing on the dielectric properties of these materials, is the densification behaviour and associated microstructure development of the ceramics (Fig. 2.16) using various additives that form liquid phase at low temperatures. Normally, the perovskite solid solutions are sintered at temperature between 1200 and 1300 °C to obtain a densified product exhibiting superior dielectric properties. Guha *et al.*[107] reported that the optimum conditions for obtaining PMN-PT ceramics with high densities and improved dielectric properties were a nominal addition of 1 wt% exess PbO which contributed to a homogeneous distribution of PbO, and saturation with PbO throughout the grains. In most cases, minor additions of excess MgO and/or PbO are used as additives to enhance the densification process, which in turn, results in an enhancement of the dielectric properties of the sintered materials.[98,107] It has been observed that when minor amounts of excess MgO are added to a stoichiometric solid solution composition, the fraction of the undesirable pyrochlore phase is reduced and thus, the proportion of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase in the final product is substantially increased. However, this finding has been contradicted in recent study[108] in which it has been reported that an addition of excess MgO neither enhances the reaction process nor does it help in obtaining a phase-pure perovskite solid solution. In another study,[108] it has been reported that large additions of excess MgO (≈ 4 mol%) give rise to the formation of $Mg_4Nb_2O_9$, the presence of which in the sintered ceramics leads to a degradation of the dielectric properties of the materials.

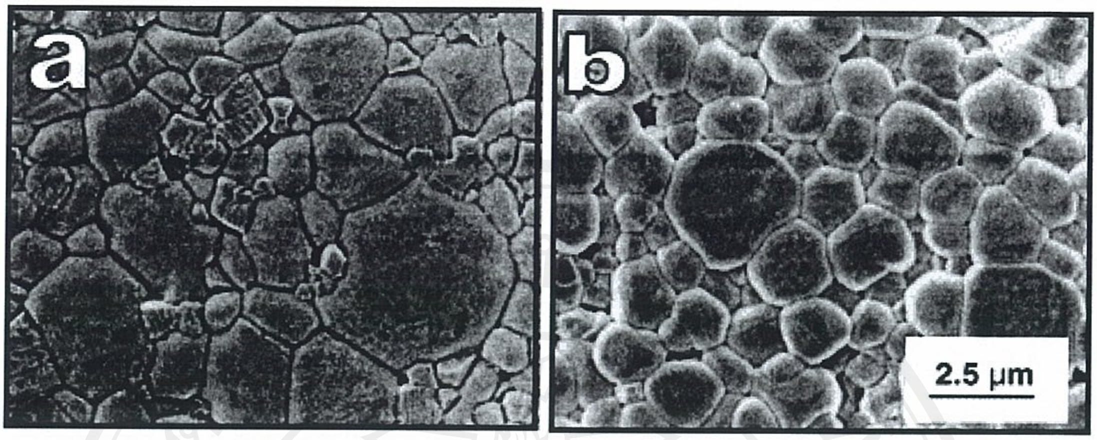


Fig. 2.16 Microstructure of (a) 0.9PMN-0.1PT and (b) 0.65PMN-0.35PT ceramics sintered at 1100 °C for 2 h.[106]

Numerous studies have been carried out so far to densify $Pb(Mg_{1/3}Nb_{2/3})O_3$–based solid solutions with minor additions of excess PbO.[107, 109-110] In these studies, it has been generally observed that the addition of excess PbO to the solid solutions results in the formation of a low-temperature melting PbO-rich liquid phase below the melting point of PbO (886 °C). The liquid thus formed spreads in the grain boundaries of the ceramics and causes an enhancement of the sintering process with rapid grain growth. However, with the formation of this liquid phase, PbO starts to volatilise off from the specimens and leads to a compositional change, which adversely affects the dielectric properties of the ceramics. Thus, widespread use of PbO as a sintering aid has not been considered as a viable means for the enhancement of the dielectric properties of the solid solutions.

Although the beneficial effects of minor additions of excess MgO and PbO on the dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-based perovskite solid solutions have been extensively investigated, little is known so far on the effect of simultaneous additions of MgO and PbO on the sintering characteristics, microstructure development and dielectric properties of these materials. In an attempt to develop low-temperature sintered $Pb(Mg_{1/3}Nb_{2/3})O_3$-based materials with minor additions of excess

MgO and/or PbO,[111] it has been found that excess MgO partly dissolves in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ perovskite structure, while the major portion of MgO remains as a second phase in the grain boundaries of the solid solutions. In another study,[112] it has been observed that sintering $Pb(Mg_{1/3}Nb_{2/3})O_3$-based materials with excess MgO and PbO results in an increase in the fluidity of the liquid phase at 950 °C and leads to an enhancement of the densification process. However, it should be note that sintering of ceramics to a high density in presence of a liquid phase is not always the objective for obtaining superior dielectric properties of capacitor materials. On the other hand, formation of equilibrium phase assemblages with minor additions of the one or more secondary phases and optimizing the sintering conditions are far more important for the development of a homogeneous microstructure exhibiting desired grain morphology and grain boundary characteristics with superior dielectric properties.

In the present work, a complex perovskite solid solution having a composition (1-*x*)PMN-(*x*)PT was prepared from the B-site precursor technique and then sintered under various firing conditions. The phase formation characteristics, densification behaviour and microstructure development of the sintered specimens were studied and the data thus obtained correlated with the adopted processes.