CHAPTER 2

LITERATURE REVIEW

In this chapter, attention is focused on the perovskite ferroelectrics in the lead magnesium niobate-lead titanate system. It is first necessary to describe the information background of perovskite ferroelectrics. The relevant literatures on phase formation, microstructure and dielectric properties of PMN, PT and PMN-PT are reviewed with attention paid on their processing-microstructure-dielectric properties relationships. Finally, the concept of ceramic nanocomposites is then described in more details.

2.1 Perovskite Ferroelectrics

The perovskite structure is one of the most technologically important structure type in materials science [1]. Numbers of the perovskite family include relaxor ferroelectric materials, superconducting materials, microwave dielectric materials, magnetic materials, magnetoresistive materials, non-linear optical materials, catalyst materials and thermoelectric materials. Furthermore, the vast majority of technologically important ferroelectric/piezoelectric materials belong to the perovskite family. The following sections describe the crystal structure and phase stability for oxide perovskite strucutures.

The perfect prototype perovskite is generally described as having simple cubic structure and takes its name from the isostructural mineral "perovskite" calcium titanate, $CaTiO_3$ [8]. However the cubic structure is better described by $SrTiO_3$ [9,10]. The cubic prototype $SrTiO_3$ has a space group *Pm3m* with the titanium atoms located

at the corners of the unit cell cube, the strontium atom located at the center of the cube and oxygen atoms are placed at the centers of the twelve cube edges (Fig. 2.1 (a)). The first alternative is a cubic cell that has the titanium atom at the center, the strontium atoms are on the cell corners and the oxygen atoms are on the cell faces (Fig. 2.1 (b)). The perovskite structure can therefore be represented as linked framework of BO₆ (TiO₆) octahedral with the A-site ion in 12-fold coordination with oxygen and the B-site in 6-fold coordination. In most cases the cubic structure in Fig. 2.1 is somewhat ideal. The structural formula is often referred to as:

In which the A atoms are in 12-fold coordination and both the B and X atoms are in 6-fold coordination.

 $A^{(XII)}B^{(VI)}X_3^{(VI)}$

(2.1)



Fig. 2.1 Two alternative representations of the perovskite (ABO₃) structure (gray solid = A, black solid = B and red solid = O).

The perovskite structure is tolerant of a very wide range of multiple cation substitutions on both the A- and B-sites. The anions and cations can be interchanged with ions of different valences, as long as charge neutrality is maintained. The first of the three major variations is the $A^{1+}B^{5+}O_3$ family, as example of which is KNbO₃. The best studied family is probably $A^{2+}B^{4+}O_3$, which include PbTiO₃ and BaTiO₃. Finally, is $A^{3+}B^{3+}O_3$ family, such as BiFeO₃ and BiScO₃.

In addition to these three families, there are a wide variety of complex perovskite forms resulting from multiple ionic substitutions. The general formula for the complex perovskite is

$$(A'A'')^{(XII)}(B'B'')^{(VI)}X_3^{(VI)}$$

(2.2)

The A' and A" cation sites typically contain Pb²⁺, Ba²⁺, Sr²⁺, Bi²⁺ or La³⁺; the X anion site is generally occupied by oxygen; and the B' and B" cation sites can contain a great variety of cation. The B' site is usually occupied by a lower valence cation, such as Mg²⁺, Ni²⁺, Zn²⁺, Fe³⁺ or Sc³⁺. The B" site is typically highly-charged ions such as Ti⁴⁺, Nb⁵⁺, Ta⁵⁺ or W⁶⁺.

These substitutions generally lead to there major complex perovskite subfamilies: $A^{2+}(B^{3+}_{1/2}B^{5+}_{1/2})O_3$, $A^{2+}(B^{2+}_{1/2}B^{6+}_{1/2})O_3$ and $A^{2+}(B^{2+}_{1/3}B^{5+}_{2/3})O_3$. Most relaxor ferroelectrics are rhombohedral perovskite, however, in many cases the symmetry is described as pseudo-cubic due to a lack of long-range global order [11].

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 [12,13]. Relaxors show several intriguing phenomena which clearly distinguish them from the normal ferroelectrics, Table 2.1 and 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 behavior of relaxors coupled with their desirable volumetric efficiencies has pushed much research in the direction of compositional design [1,12,14]. 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.

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 Table 2.1 Property differences between normal and relaxor perovskite ferroelectrics [1].

	9181819 B	
Properties	Normal ferroelectrics	Relaxor ferroelectrics
Permittivity temperature dependence $\varepsilon = \varepsilon(T)$	Sharp 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 \rightarrow ferroelectric phase	No X-ray line splitting, giving a pseodu-cubic structure



Fig. 2.2 (a) Normal [15] and (b) relaxor ferroelectric behavior [1] (ε_r = dielectric constant and tan δ = dielectric loss).

2.1.1 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 [14] in the late 1950s and is one of the most studied of the complex lead-based perovskites. At room temperature, PMN exhibits a cubic perovskite structure with space group *Pm3m* and lattice constant *a* = 4.04 Å [15]. 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 [16].

Pure lead magnesium niobate (PMN) [17,18] is a representative of relaxor ferroelectric materials with a transition temperature of -10 °C, at 1 kHz. There is cation disorder in the *B*-site for Pb(Mg_{1/3}Nb_{2/3})O₃ [19-21]. The composition regarding Mg/Nb ratio is not stoichiometric in the micro/nano-regions, leading to different ferroelectric transition temperatures which enhances the dielectric peak broadening. However, there have been many models proposed to explain the behavior of the relaxor ferroelectric, for example, the inhomogeneous micro/nano-region model, the micro-micro domain transition model, the superparaelectric model, the dipolar glass model, the order-disorder model and etc. [21-24].

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 Nb₂O₅, the product obtained via single step mixed oxide reactions is nearly unavoidably a cubic pyrochlore of type Pb₃Nb₄O₁₃ or a rhombohedral pyrochlore of the type Pb₂Nb₂O₇, both of which are greatly detrimental to dielectric and piezoelectric properties.

From Inada's work [25], it is clear that the formation of perovskite PMN is directly related to the reactivity of the oxide MgO (or in the case of other relaxors the B'-site cations), relative to that of other phases in the binary system PbO-Nb₂O₅ (Fig. 2.3). The initial reaction between PbO and Nb₂O₅ results in the formation of cubic pyrochlore (Pb₃Nb₄O₁₃ or P₃N₄), where upon further reaction with PbO results in the formation of a rhombohedral pyrochlore Pb₂Nb₂O₇ (P₂N₂). The rhombohedral pyrochlore then reacts with MgO at higher temperature to form perovskite PMN, with the reappearance of cubic pyrochlore phase. Thus, to obtain single-phase PMN, it is necessary to prevent the evaporation of PbO, which would slow down these reactions, and to repeat the process of crushing, and calcination.

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Fig. 2.3 System PbO-MgO-Nb₂O₅, M = MgO; P = PbO; $N = Nb_2O_5$; Pyc ss = pyrochlore solid solution [26].

Lejeune and Boilot [27] have reported a somewhat different reaction sequence for the formation of PMN. They have found that the reaction of PbO and Nb₂O₅ leads to the formation of three types of pyrochlore phases, Pb₂Nb₂O₇ and Pb₃Nb₄O₁₃ and further reaction between P₂N₂ with PbO forms a lead-rich P₂N₂ pyrochlore with the P₃N₄ cubic pyrochlore phase being stable. At about 830 °C, a liquid phase was found to form and P₂N₂ reacted with MgO to form perovskite PMN with the P₃N₄ phase being unaltered.

Another interesting reaction sequence for the formation of PMN was also introduced by Swartz and Shrout [28]. In their work, only the cubic pyrochlore P_3N_4 was observed, which in turn reacted with PbO and MgO to form perovskite PMN. They also confirmed that MgO was incorporated into the cubic pyrochlore structure having an approximate formular of Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}. The exact amount of MgO that can be incorporated into the pyrochlore structure is not yet known. Several researchers [17,29,30] have also reported the partial incorporation of MgO in the pyrochlore phase with a similar composition. These literatures indicated that PMN does not form by a direct reaction of the oxides but by subsequent reactions through pyrochlore phases, therefore, the cubic pyrochlore is very stable and is never completely eliminated. Also, the formation of PMN could be accelerated by addition of excess PbO and MgO [29,30]. Difference reaction sequences in the formation of PMN could be due to the dependence of reaction kinetics on various processing parameters, such as particle size and surface area of the raw materials, heat treatment and etc. [28,30].

To obtain stoichiometric perovskite PMN, the intermediate pyrochlore phase reaction must be eliminated. Thus, an alternative approach was devised, whereby the two refractory *B*-site oxides, MgO and Nb₂O₅, were pre-reacted to form the columbite MgNb₂O₆ before reaction with PbO as shown [28]:

$$MgO + Nb_2O_5 \rightarrow MgNb_2O_6 : \sim 1000 \ ^{\circ}C$$
(2.3)

$$MgNb_2O_6 + 3PbO \rightarrow 3Pb(Mg_{1/3}Nb_{2/3})O_3 : \sim 700 \ ^{\circ}C$$
 (2.4)

In this reaction sequence, the pyrochlore formation is bypassed, leading to the direct formation of PMN. Naturally the success of this approach depends on various processing parameters, such as reactivity of MgO, degree of mixing, control of PbO volatility, and the reversibility of reaction (Eq. 2.4). It has been confirmed by many

researchers [26-31] that pyrochlore-free PMN phase, can be achieved by employing this method.

Effect of various processing parameters on the composition and amount of phases formed in the preparation of PMN has been investigated by Lejeune and Boilot [27,32]. Results of various ceramic processing studies are given in Table. 2.2. As expected, reaction sequences (Eq. 2.3) through (Eq. 2.4), process that reduce the volatility of PbO, such as shorter sintering time and closed crucible firing, lead to an increased amount of perovskite phase. Conversely, process that lead to PbO loss such as prolong firing, leads to an increased amount of pyrochlore phase, as is evident from the following reverse reaction:

$$6Pb(Mg_{1/3}Nb_{2/3})O_3 \to Pb_3Nb_4O_{13} + 3PbO + 2MgO$$
(2.5)

From this reaction as well as other reactions in which a pyrochlore phase forms, free PbO will be presented in the ceramic unless driven off through volatilization. The presence of free PbO is commonly observed at the grain boundaries and at triple points. It is believed that this relatively weak amorphous PbO grain boundary phase gives rise to the characteristic intergranular fracture frequently observed in relaxors. Along with the amorphous PbO at the grain boundary, small grains of pyrochlore are also observed. It has been reported that, depending on the ceramic process, a pyrochlore phase can also exist in the form of large discrete grains, as example shown in Fig. 2.4.



Fig. 2.4 As-fired surface of PMN ceramic indicating the existence of pyrochlore (Pyro) and MgO phases [29].

From Table 2.2, it is seen that the reactivity of raw material, firing condition and atmosphere can be modified to enhance the yield of perovskite PMN. To eliminate the pyrochlore phase completely, it has been shown that an addition of up to 6 wt% excess PbO is necessary [33]. Excess PbO accelerates the formation of the PbO rich pyrochlore phases, P₂N₂ and P₃N₂. The addition of excess MgO (at least 5 mol%) also helps to eliminate the pyrochlore phase by compensating for poor dispersibility and reactivity [33]. The PMN perovskite phase will be nonstoichiometric, which is not desirable. The importance of obtaining a stoichiometric perovskite PMN composition is evident by the vast variation in physical and dielectric properties reported for PMN in Table 2.3. It is clear that PbO and MgO deficiency can result in an excessive amount of pyrochlore phase which causes poor densification and greatly degraded dielectric properties. Discreate grains of pyrochlore phases ($\varepsilon_r \sim 120$) would have little effect on the dielectric properties of relaxor, but presence of free PbO ($\varepsilon_r \sim 20$) in the grain boundary will lower the overall dielectric constant, giving rise to the observed grain size dependency of ε_r [35].

Process	Parameter	Perovskite	Comment					
		PMN (wt%)						
Raw material	$MgO \rightarrow MgCO_3$	$42 \rightarrow 81$	Improved reactivity					
Solvent	Water \rightarrow acetone	51 → 81	Improved dispersability					
Calcination	Cycle 1 to 3	$60 \rightarrow 90$	Help prevent anion					
	$800 \rightarrow 1000 \ ^{\circ}C$	$68 \rightarrow 76$	deficient pyrochlore					
	Air O ₂	$77 \rightarrow 85$	formation					
Sintering Condition	Dwell time $6 \rightarrow 24$ h at 1050 °C	$81 \rightarrow 60$	PbO loss					
	Heating rate 770 \rightarrow 5 °C/min	$49 \rightarrow 77$						
	Open \rightarrow close crucible	$33 \rightarrow 80$	PbO loss					
	i g h t s	r e s	erved					

Table 2.2 Influence of processing parameters on PMN formation [32].

 Table 2.3 Effect of nonstoichiometry on the dielectric properties of PMN ceramics
 [36,37].

Parameter	Effect	Comment			
PbO deficiency	Reduction in ε_r	Promotes formation of pyrochlore			
		and poor densification			
MgO deficiency	Reduction in ε_r	Promotes pyrochlore			
PbO excess	Reduction in ε_r	Excess PbO in grain boundary			
	Insulation resistance (IR)				
	degraded				
	Enhanced ε_r and IR	Promotes densification and			
	Increase in aging	perovskite phase			
MgO excess	Increase in ε_r	Promotes grain growth and			
		elimination of pyrochlore phase			

ลิ<mark>ปสิทธิ์มหาวิทยาลัยเชียงใหม่</mark> Copyright[©] by Chiang Mai University All rights reserved The effect of different solid-state reaction route on the formation of perovskite PMN is compared as shown in Table 2.4

Preparation Method	Calcination	PMN (wt%)	References
	Temperature		
	remperature		
	(°C)		
Conventional mixed-oxide	700-800	<70	[23]
Conventional mixed-oxide	700-800	\$70	[23]
MgCO ₂ precursor	1000	81	5 [31]
MgCO3 precursor	1000	01	205[31]
R_site precursor	Step 1: ~1000		
D-site precuisor	Step 1. 1000		
(Columbite)	Step 2: ~700	100	[27]
<i>B</i> -site precursor	900	100	[43]
(Corundum)			
(Corundum)			

Table 2.4 The effect of various mixed-oxide methods on PMN formation.

Recent work on the preparation of PMN [38,39], has also shown that another *B*-site precursor method $Mg_4Nb_2O_9$ (corundum-type) is a better precursor than the columbite $MgNb_2O_6$ for the successful preparation of single phase perovskite PMN [1,12,13], when MgO and Nb₂O₅ are reacted with 1:1 stoichiometry, a small amount of $Mg_4Nb_2O_9$ is formed along with the columbite precursor MgNb₂O₆, which in turn leads to the formation of a minor amount of "free Nb₂O₅" in the precursor. This may

be the reason for the formation of small amount of pyrochlore phase when the synthesis of PMN is carried out using the columbite precursor. And it has been found that the perovskite phase can easily be stabilized by using corundum besides columbite $MgNb_2O_6$.

So far, several efforts [40-44] have been made to enhance processing techniques to create or develop materials with properties approaching applicational requirements. These include (a) use of a two stage calcination route [28,40]; (b) using higher purity and finer, more reactive precursor powders [43]; (c) employing additives [41,42] and (d) carrying out repeated calcination and milling cycles [32,44]. These techniques affect the phase formation, structure and dielectric properties of materials in different ways. Amongst all the issues reported so far, most attention has been concentrated on the powder processing stage, whereas investigations of modified sintering techniques have not been widely carried out.

Two alternative techniques employing longer heat treatment, whilst reducing the firing temperature, were reported by Lejeune and Boilot [45] for PMN ceramics. The repeated calcination stage, corresponding to the so-called double calcination technique, demonstrated the possibility of obtaining single-phase PMN powder. The second technique, paid attention to three sintering cycles (either 1000 °C for 6 h or heating to 800/830 °C followed by cooling down and heating to 1000 °C again for 6 h. The second sintering cycle (i.e. heating to 800 °C) was found to produce PMN ceramic with the best dielectric properties.

In 1999, Ananta and Thomas [4] attempted to fabricate PMN ceramics by using a two-stage sintering technique (Fig. 2.5). Instead of using a single, high firing temperature or a long soaking time, two moderate temperatures were adopted. They have demonstrated that under suitable conditions, the properties of the PMN ceramics may be equivalent to those obtained from a single sintering stage (Figs. 2.6 and 2.7). Thus sintering is a crucial stage which can influence the dielectric properties of the final product more strongly than the choice of reaction precursors. This is because pyrochlore formation and lead volatilisation can easily become the predominant considerations for lead-based complex perovskite materials.



Fig. 2.5 Preparation of PMN ceramics employing a two-stage sintering method [4].

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Fig. 2.6 XRD patterns of PMN ceramics sintered at (a) 1025 °C, (b) 1025/1050 °C, (c) 1025/1100 °C, (d) 1025/1150 °C and (e) 1025/1200 °C, for constant dwell times of 2 h at each stage [4].



Fig. 2.7 SEM micrographs of as-fired surface of PMN ceramics sintered at (a) 1025 °C, (b) 1025/1100 °C, (c) and (d) 1025/1200 °C, for constant dwell times of 2 h at each stage [4].

Since the preparation of pure perovskite PMN is relatively difficult via conventional solid-state reaction route, in this work, attempt has been made to produce pure, dense PMN ceramics by using the B-site precursor method. This study was also under taken to further examine the inter-relationships between processing, phase formation, microstructure and dielectric properties of PMN ceramics.

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2.1.2 Lead titanate (PT)

Lead titanate (PbTiO₃ 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 [15]. 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 ($c_r \sim 200$), pyroelectric, and piezoelectric ($k_r/k_p > 10$) properties [1,12,15]. It has been extensively employed to make solid solutions with lead zirconate (PbZrO₃) to obtain lead zirconate titanate (PZT) material [12] and also other perovskites, forming a wide range of versatile crystalline solid solutions, such as Pb(Mg_{1/3}Nb_{2/3})O₃- PbTiO₃ or PMN-PT and Pb(Zn_{1/3}Nb_{2/3})O₃- PbTiO₃ or PZN-PT [1,12]. 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. 2.8).

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 PbTiO₃ powders at lower temperatures having controlled physical and chemical characteristics [46-49]. Many investigations have thus focused on the processing of PT powders via several preparation routes, such as mixed oxide [46], sol-gel [47], coprecipitation [48], hydrothermal reaction [49], 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. 2.8 Variety of ferroelectric PT-based ceramics used in electronic applications [12].

The stoichiometry of PbTiO₃ is known to be an important factor for ensuring good electrical characteristics [1,12]. Generally, the conventional method adopted for its preparation involves the heating of mixture of lead oxide and titanium oxide above 1000 $^{\circ}$ C [50], a temperature significantly above the melting point of PbO, which usually leads to Pb-deficient PbTiO₃ [51]. The phase equilibria in PbO-TiO₂ system is

shown in Fig. 2.9. It is seen that $PbTiO_3$ forms from solid-state reaction of PbO and TiO₂ as low as 360-375 °C and has two eutectics [15].



Fig. 2.9 Phase equilibria in the system PbO-TiO₂ [15].

In 1996, Pillai and Ravindran [46] have undertaken a systematic study of the reaction between PbO and TiO₂ using DTA and XRD techniques. 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 PbTiO₃ compound has been directed towards

determining sintering behavior [52] and electrical properties [53]. Only limited attempts have been made to improve the yield of PT optimising processing steps.

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 [54]. Fang *et al.* [48] reported that the formation temperature for a single tetragonal PT phase via the co-precipitation route is as low as 500 °C, which is lower than those reported for most chemistry-based routes such as sol-gel technique [47]. However, the method did not give reproducible powders due to a thermodynamical preference for precipitation of lead oxalate and titanium hydroxide separately [48].

The sol-gel route is well suited to the preparation of powders and thin films of PT [55-57]. 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 [55,56] and subsequently transform to perovskite at higher (500-700 °C) temperatures. Calzada *et al.* [54] reported that the formation of pyrochlore, a metastable intermediate phase, and/or lead-deficient secondary phases, PbTi₃O₇, delay the formation of perovskite phase and can damage significantly the electrical properties. Several researchers have synthesized crystalline PT in a two-step process, i.e. by homogeneously precipitating a precursor salt at low temperatures and

calcining it to form PbTiO₃ at higher temperatures. Fox *et al.* [58] precipitate an amorphous precursor powder at ~ 50 °C using Pb(NO₃)₂ and TiCl₄ with the addition of NH_{3(aq)} and H₂O₂. The powder was calcined at 600 °C. Greninger *et al.* [59] reported a similar synthesis using TiCl₄, Pb(NO₃)₂ or PbCl₂, H₂O₂ 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.

More recently, mechanochemical synthetic route has been applied to prepare a few ferroelectric powders, although in many cases it was not very successful [60,61]. 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.* [62] 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.

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. Hydrothermal synthesis of PT powders has several advantages over coprecipitation and sol-gel methods. The influence of different alkali reagents and their concentration on phase formation (Fig. 2.10) and crystallite morphology (Fig. 2.11) of the hydrothermally derived PT powders was investigated by Rujiwatra *et al.* [63]. They have demonstrated that the excess of the alkali hydroxide over ammonium hydroxide in the reaction mixtures always led to the formation of tetragonal perovskite PT in *P4mmm* symmetry, independently from the presence of ammonia.



Fig. 2.10 Powder XRD patterns of tetragonal phase-pure perovskite PT synthesized under hydrothermal pressure at 180 °C using (a) only KOH [4 mol dm⁻³] for 3 h compared to those using KOH [4 mol dm⁻³] and 30% ammonia solution for (b) 3 h (c) 6 h, and (d) KOH [4 mol dm⁻³] and 15% ammonia solution for 12 h, as well as (e) NaOH [4 mol dm⁻³] and 30% ammonia solution for 6 h [63].



Fig. 2.11 The electron micrographs showing various types of morphologies of the powders obtained from the reactions using 30% ammonia with the addition of (a) KOH [4 mol dm⁻³] for 3 h (b) KOH [1 mol dm⁻³] for 2 h, (c) NaOH [1 mol dm⁻³] for 12 h, and (d) that without using any alkali hydroxide for 12 h [63].

In general, the overriding aim of any materials processing technique is to achieve a final product with consistent properties. The mixed oxide synthetic route is probably one of the most fundamental, practical routine methods which have 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 as example revealed by Udomporn *et al.* [64] (Figs. 2.12 and 2.13). Although some research has been done in the preparation of PT powders via a mechanical milling technique [46,64], a systematic study regarding the influence of milling time on the preparation of PT powders has not yet been widely reported.



Fig. 2.12 XRD patterns of PT powder calcined at 600 °C for 1 h with various heating/cooling rates [64].



Fig. 2.13 SEM micrographs of the PT powders calcined at (a) 600 °C/1h, (b) 550 °C/4h, (c) 700 °C/1h and (d) 800 °C/1h, with heating/cooling rates of 20 °C/min [68].

For PT ceramics, it is well known that preparation of pure, dense PbTiO₃ 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 [50]. 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 [65]. 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 [66]. Because a large lattice anisotropy exists, a

very high electric field and high temperature are required for their poling [67]. 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 [66-69]. Other additives, such as Bi and Y, were also successfully used to improve the properties of PT ceramics [70]. Futhermore, addition of these ions lowers the sintering temperature and consequently suppresses lead volatilization. Substitution into the Ti⁴⁺ sites by Mn⁴⁺ enhances resistivity by compensating charges due to off-valence substitution for Pb²⁺sites. As a result, modified PbTiO₃ ceramics can be subjected to severe poling conditions, and saturated piezoelectric properties can be obtained [66].

Besides having a high Curie temperature and a low dielectric constant, modified PbTiO₃ ceramics possess 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 [66,71].

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 [72].

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 [73]. Lead titanate has been reported to crack spontaneously when the average grain size is larger than $\sim 3 \,\mu\text{m}$ and to completely disintegrate into powders when the grains are larger than 10 μ m [74]. Therefore, one plausible way to fabricate pure PT ceramics with lower internal stress is to reduce the grain size (below 3 μ m); the binding force between the grains may increase with the relative area of the grain boundaries [75]. However, dense ceramics with fine grains (< 3 μ m) are difficult to prepare via conventional sintering processes.

Kim *et al.* [76] 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 μ m and 1.8 μ m, respectively. Recently, Kong *et al.* [77] have applied a high-energy ball milling technique to the mixture of PbO and TiO₂ for 20 h and have obtained dense PT ceramics with submicrometer-sized grains (< 1.5 μ m), as shown in Fig. 2.14.

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Fig. 2.14 The surface microstructure of the PbTiO₃ ceramics sintered at 1100 °C for (a) 20 h (b) 40 h (c) 60 h and (d) 80 h [77].

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 Sasaki [75] 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 MnO₂ doped ceramics sintered at 1130 °C was mechanically strong but was fragile when sintered at 1150 °C. Ishikawa *et al.* [78] 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 μ m and then remain constant. This has been explained as the contribution of strong depolarization making the ferroelectric phase unstable, particularly in thin films. From Table 2.5, it is seen that the preparation method and sintering condition can be modified to enhance the production of perovskite PT.

Preparation	Sintering	Dwell Time	Relative	References
Method	Temperature	(h)	Density	
	(°C)		(%)	
Mixed-oxide	1100		95-96	[79]
Sol-gel	1100	0.5	96	[50]
Spark plasma	900 -1100		69-98	[79]
sintering				
WO_6 and Fe_2O_3	1225-1230	2	95-97	[80]
dopant				

Table 2.5 Influence of processing parameters on PT densification.

Udomporn *et al.* [81] have demonstrated that the highly dense and stable PT ceramics fabricated via a normal sintering method were successfully formed by the careful control of processing parameters. It has been observed that the slow heating/cooling rates are important parameters in preparing dense PT ceramics. The well defined-grain ceramics with the average grain size of about 0.6 μ m could be prepared by heating them to 1225 °C using the considerably slow heating/cooling

rates of 1 °C/min and dwell time of 2 h. Moreover, it was also found that the relative densities of these ceramics would be as high as 97%.

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.



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2.1.3 Lead magnesium niobate-Lead titanate (PMN-PT)

During several past decades, many experiment [82-84] studies were carried out on various phase transformation and crystal structures of lead-based solid solutions consisting of normal and relaxor perovskite ferroelectrics. 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 [2,13]. 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 behavior have a nanometer scale heterogeneity in composition [85,86]. In the 1950s, Smolenski and coworkers [15,16] investigated many cation substitutions into PbTiO₃ 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 Ti⁴⁺ ion and the combination must yield the same average charge as Ti⁴⁺ to maintain charge neutrality. Many such compositions take on the complex perovskite structure, and their properties have been extensively reported by several researchers [87-89].

Lead magnesium niobate (PMN) is nowadays acknowledged as the representative of relaxor ferroelectrics [14]. 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 [87]. Though the Curie temperature or better yet, Curie range of PMN is well below room temperature where 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 [88].

The (1-x)PMN-(x)PT system also show a morphotropic phase boundary (MPB) near $x \sim 0.34$, separating pseudo-cubic phase and tetragonal phases (Fig. 2.15) [88]. 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. 2.16. These properties make the materials particularly suitable for use in electrostrictive actuator, sensor and piezoelectric devices.

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Fig. 2.15 Phase diagram of the solid-solution of the PMN-PT system showing the morphotropic phase boundary (solid circles = calculated data and open circles = experimental data) [88].



Fig. 2.16 Dielectric behaviour of (1-x)PMN-*x*PT ceramics (at 1 kHz) as a function of temperature [88].

There are several [89-99] 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 0.9PMN-0.1PT, 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 [88]. For this composition, the temperature of polarization loss is ~ 10 °C; hence, the material is a relaxor at room temperature (25 °C).

It is also an attractive replacement for BaTiO₃ in multilayer capacitors because it can be sintered at low temperature in comparison to BaTiO₃ [95,96]. This powder has a vast promise for making polymer composite as a dielectric material in high performance capacitors. Takeuchi *et al.* [92] 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 0.9PMN-0.1PT 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.* [93] investigated PMN-PT materials for medical ultrasonic transducer applications. 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 compositions 0.93PMN-

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0.07PT [94] and 0.65PMN-0.35PT have been shown to exhibit the piezoelectric properties suitable for smart ferroic systems such as vibration control, actuator and sensor applications [95,96].

In 1989, Choi *et al.* [89] 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-solution 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 2.6. 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.* [97] reported their study on the dielectric and piezoelectric properties of (1-x)PMN:(x)PT across a compositional range which includes the MPB ($0 \le x \le 0.5$). The composition 0.95PMN-0.05PT has been shown to exhibit great promise for sensor and actuator applications. It has been found that the transition temperature of 0.95PMN-0.05PT ceramics (~ 20 °C) is closest to room temperature and thus showed the highest room temperature dielectric constant, consistent with Choi *et al.* [87] and Kelly *et al.* [96]. 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 [97] 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.

Structural studies of PMN as a function of PT content have been reported by Viehland *et al.* [98]. 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%. Other studies by Chen *et al.* [99] and Randall *et al.* [100] 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 superlattice reflections. These ordered regions did not coarsen on heat treatment [101]. Furthermore, Chen *et al.* [99] 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.

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Sample	Unpoled				7	Poled						
x	Er	$tan\delta$	Er, max	$T_{\rm C}(^{\circ}{\rm C})$	$ an \delta_{ m max}$	d ₃₃	Er	$tan\delta$	E _{r, max}	$T_{\rm C}(^{\rm o}{\rm C})$	$ an \delta_{ m max}$	d ₃₃
0.225	3533	0.032	29552	112	0.036	297	1695	0.022	28688	114	0.042	96
0.25	2778	0.031	30192	127	0.061	305	2435	0.018	28714	130	0.072	124
0.275	2873	0.035	33432	136	0.045	353	2091	0.030	31986	138	0.051	130
0.3	3782	0.034	36469	139	0.035	669	4936	0.027	33289	143	0.057	136
0.325	4170	0.029	33350	155	0.029	663	5260	0.018	30048	159	0.049	156
0.35	3190	0.013	30623	177	0.098	456	3119	0.006	29020	182	0.069	230
0.375	2434	0.015	28524	190	0.018	405	2781	0.011	28126	198	0.038	191
0.4	2097	0.016	27156	202	0.030	323	2371	0.010	25189	207	0.044	204
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Table 2.6 Dielectric and piezoelectric properties of (1-*x*) PMN: *x* PT [89].

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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 PMN-PT formation of an unwanted pyrochlore phase has long been recognized as a major problem [102-104]. The presence of the pyrochlore phase in the sintered ceramics, even in small quantities, has been associated with inferior dielectric properties of the materials [105,106]. 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 [107], has been widely used in the synthesis of phase-pure perovskite PMN-based materials. During the last several years, numerous studies [105,106] 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 [107] in which prefabricated Pb₃Nb₂O₈ 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 PMN.

Several methods such as co-precipitation, sol-gel, gel combustion, and a molten salt method have been developed to prepare pyrochlore-free PMN-PT compounds [108-111]. Although these chemical 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 [90], 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 0.9PMN-0.1PT and 0.65PMN-0.35PT powders after milling for only 2 h (Fig. 2.17) [112].



Fig. 2.17 XRD patterns for the mixed oxide mixtures: (a) 0.9PMN-0.1PT and (b) 0.65PMN-0.35PT milled for 2 h [112].

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 PMN-PT solid solutions, another area of concern, which has an important bearing on the dielectric properties of these materials, is the densification behavior and associated

microstructure development of the ceramics (Fig. 2.18) using various additives that form liquid phase at low temperatures. Normally, the PMN-PT solid solutions are sintered at temperature between 1200 °C and 1300 °C to obtain a densified product exhibiting superior dielectric properties. Guha et al. [113] 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 [104,113]. 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 PMN phase in the final product is substantially increased. However, this finding has been contradicted in recent study 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 [114], it has been reported that large additions of excess MgO ($\approx 4 \text{ mol}\%$) give rise to the formation of Mg₄Nb₂O₉, the presence of which in the sintered ceramics leads to a degradation of the dielectric properties of the materials.



Fig. 2.18 Microstructure of (a) 0.9PMN-0.1PT and (b) 0.65PMN-0.35PT ceramics, sintered at 1100 °C for 2 h [112].

Numerous studies have been carried out so far to densify PMN-PT solid solutions with minor additions of excess PbO [113,115,116]. 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 PMN-based 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 PMN-based materials with minor additions of excess MgO and/or PbO [117], it has been found that excess MgO partly dissolves in the PMN perovskite structure, while the major portion of MgO remains as a second phase in the grain boundaries of the solid solutions. In another study [118], it has been observed that sintering PMN-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 behavior and microstructure development of the sintered specimens were studied and the data thus obtained correlated with the adopted processes.

2.2 Ceramic Nanocomposites

Research and development in the field of electroceramics are driven by technology and device applications. It includes research on a broad spectrum of the inorganic materials, it covers all scales from the level of the crystalline lattice to that of final devices. The applications find a place in an increasing number of domains, ranging from environment monitoring and transportation, through medicine and health-care, to electronics and communications. Two tendencies are emerging: surface and interface phenomena play an increasingly important role, motivated by the interest to integrate electroceramic functions into microelectronics and Micro-Electro-Mechanical Systems (MEMS) technologies as well as by the evolution of bulk products from discrete components into material systems. Electroceramics are following conventional semiconductors with respect to down-scaling. Nano-size effect, nanotechnology related processes and the use of new characterization techniques to reveal nanometric scale features are therefore gaining in importance.

2.2.1 Nanocomposites

Composite materials prepared to have inhomogeneity in smaller scale than submicron (10^{-7} m) are called nanocomposites. Nanocomposite materials are known to posses unique physical and mechanical properties, including enhanced ductility and superplasticity [119], even in traditional brittle materials, superior strength and optical transparency in usually opaque [120,121]. Ceramic nanocomposites were first officially reported by Niihara *et al.* [122] in 1991 and are formed by the addition of ultra-fine

particles, which are typically below 100 nm, to a ceramic matrix. Since the concept of designing ceramics using the "*nanocomposites*" route was proposed, there has been continued interest into the use of fine particles to improve a variety of properties. The possible structures that are formed by the addition of nano-particles are divided into 4 types based on matrix grain size and secondary-phase particle size, i.e. intergranular, inter-intra-granular and nano/nanocomposites as shown in Fig. 2.19.

It is expected that resistance to high temperature creep will be improved by the intergranular structure due to grain boundary pinning. Correspondingly, the intragranular configuration hinders crack motion through the grain, i.e. transgranular fracture and potentially the strength and toughness can be enhanced. The dual composite will have the benefits of both the intergranular and intragranular arrangement, while the small grain size of the nano/nano-composite allows the opportunity of superplasticity. However, the large majority of so-called *nanocomposites* developed to date are actually *micro-nanocomposites*, rather than nano-nano composites (where both the matrix and inclusion grain sizes are in the nanometer range). Kuntz *et al.* [123], therefore, propose a reclassification of the ceramic nanocomposite models as shown in Fig. 2.20. In this new scheme, the matrix phase is continuously nanocrystalline while the second phase varies, leading to four nanocomposite models: the nano-type, the nano-micro type, the nano-fiber type and the nano-nanolaver type:

 Nano-nano composite: both the matrix and second phase have equiaxed grains of less than 100 nm;

- *Nano-micro composite*: nanocrystalline matrix and a microcrystalline second phase;
- *Nano-fiber composite*: whiskers or fibers incorporated into a nanocrystalline matrix; and

Nano-nanolayer composite: nanocrystalline matrix and a grain boundary layer of a second phase.

This classification is specifically designed for applications requiring improved fracture



Fig. 2.19 Niihara's classification as (a) intergranular, (b) intragranular, (c) inter- and intra-granular and (d) nano/nano composites structural models [125].



Fig. 2.20 Kuntz's classification of (a) nano-nano, (b) nano-micro, (c) nano-fiber and (d) nano-nanolayer composites structural models [123].

From previous works [124-127], it is seen that significant improvements in strength for some ceramic nanocomposites have been reported. For example, the strength has been improved from 683 MPa for monolithic Al₂O₃ to 1090 MPa for an Al₂O₃-15% Ni nanocomposite [124]. The similar study on mechanical properties of electroceramic nanocomposites such as BaTiO₃-based and PZT-based can be found in literatures [128-130], however, attention paid on the effect of nanometer phase on the electrical properties of these materials is lacking. Thus in this study, perovskite PMN-PT ceramic was adopted as key model for the study of microstructural engineering via ceramic

nanocomposites approach. The effect of key processing parameters on the phase formation, microstructure and electrical properties will be quantitatively evaluated and compared.

2.2.2 Perovskite ceramic nanocomposites

Perovskite based ceramic nanocomposites were found in many previous works [131-134]. Hwang et al. [131] selected MgO and BaTiO₃ as a matrix and secondary phase dispersoid and used conventional hot pressing or pulse electric current sintering (PECS) for preparing particle-dispersed ceramic nanocomposites. From X-ray diffraction analysis, no reaction phases between the matrix and BaTiO₃ were observed. Fracture surfaces of these monolithic MgO and MgO/BaTiO₃ nanocomposites sintered at 1300 °C for 10 min is shown in fig. 2.21. Fracture mode was found to be predominantly intergranular and transgranular fracture was also observed for both the monolithic MgO and MgO/BaTiO₃ nanocomposites. The BaTiO₃ dispersoid in the nanocomposite prepared by the PECS technique showed higher XRD peak splitting than that of the hotpressed nanocomposite indicating better ferroelectricity in the MgO/BaTiO₃ nanocomposites.

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Fig. 2.21 Fracture surfaces of (a) the monolithic MgO and MgO/BaTiO₃ ceramic nanocomposites with (b) 5 vol.% and (c) 20 vol.% BaTiO₃, produced by the PECS technique [131].

These researchers [130] also fabricated PZT/Ag nanocomposites by using conventional powder metallurgical method. Nano-sized silver particles less than 50 nm are homogeneously precipitated on the matrix PZT powder. From the X-ray diffraction analysis, no reaction phases between PZT and silver were observed. It was also found that adding nano-sized Ag particles enhanced the mechanical and piezoelectric properties of the PZT ceramics. In addition, they changed to adding nano-sized platinum particles into PZT [133]. Fatigue behavior of the unpoled PZT/Pt nanocomposites that contained precracks produced by Vickers indenter under electrical cyclic loading was investigated. It was found that the growth of the indentation crack was significantly reduced in the PZT/Pt nanocomposites.

Tajima *et al.* [134] studied effects of additives on mechanical and piezoelectric properties of PZT nanocomposites prepared from high purity PZT powder and small amount (0.1-1.0 vol%) of oxides (i.e. Al₂O₃, MgO, ZrO₂) with average particle sizes of 100, 15 and 50 nm. It was found that the fracture strength and hardness of PZT nanocomposites with 0.5 vol% Al₂O₃ or 0.1 vol% MgO additives were significantly improved. The reduced grain size of the nanocomposites is considered to be responsible for the excellent mechanical properties. Though the dielectric constants of the composites were decreased with an addition of Al₂O₃ or MgO, the planar electromechnical coupling factor (k_p) of MgO-added composites was higher than that of Al₂O₃-addition. Typical fracture surfaces of monolithic PZT compared with the PZT-based composites are shown in Fig. 2.22 (a-d). In monolithic PZT, the fracture mode was completely intergranular. In the composites, the fracture mode changed from intergranular to intragranular.

From these literatures, it is seen that the intergranular and intragrular types of nanocomposite structure are typical observed in the perovskite ceramic nanocomposites. The remarkable characteristics of these ceramic nanocomposites are summarized as significant or moderate improvement in mechanical properties. However, no attention has been paid directly to the electrical properties of the perovskite ceramic nanocomposites. Moreover, there are many unanswered questions regarding to the correlation between micro/nano structural development and electrical behavior of this material. Therefore, proper control of the processing condition during fabricating ceramic nanocomposite for improving properties is necessary to investigate as well as the study of electrical properties of this material.



Fig. 2.22 SEM photographs of (a) monolithic PZT, (b) PZT/0.5 vol% Al₂O₃, (c) PZT/0.1 vol% MgO and (d) PZT/0.5 vol% ZrO₂ ceramic nanocomposites [134].

In 2006, Chaisan [135] demonstrated that the microstructures and the dielectric properties of the ceramic nanocomposites are totally different from ceramic solid-

solutions in the PZT-BT system. The single phase of dense ceramics was found in solid solutions whereas two different phases are visible in the microstructure of ceramic nanocomposites (Fig. 2.23). The dielectric behavior of ceramic nanocomposites displayed superimposition of two phase transitions with lower highest value of the dielectric constant compared with the solid solutions (Fig. 2.24).





(a)

(b)



Fig. 2.23 SEM micrographs of as-fired ceramics of the sintered (1-x)PZT-xBT ceramic nanocomposites with x = (a) 0.1, (b) 0.3 and (c) 0.5 [135].



Fig. 2.24 Temperature and frequency dependences of dielectric properties of the (1-x)PZT-*x*BT ceramic nanocomposites with x = 0.1 [135].

Base on Chaisan's work, the idea of ceramic nanocomposite approach could be able to apply to other perovskite materials such as PMN-PT. In this work, the relationships between processing conditions, microstructures and electrical properties of PMN-PT ceramic nanocomposites will be established, and compared with those obtained from the conventional solid-solution approach. The effect of processing parameters on the arrangement of phases, microstructural evolution and properties of the ceramics will be carefully investigated.