

Microemulsion Processing of Lead Magnesium Niobate Powders

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Ultrafine lead magnesium niobate $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) powders have been successfully prepared via a microemulsion processing technique. By stepwise hydrolysis using aqueous ammonia as the precipitant, hydroxide precursor was obtained from nitrate solutions dispersed in the nanosized aqueous domains of a microemulsion consisting of cyclohexane, non-ionic surfactant (NP5+NP9) and an aqueous phase. Upon calcination of the microemulsion-derived precursor at 800 °C, PMN powders with 100% perovskite phase was obtained.

Key words : Lead magnesium niobate, microemulsion, perovskite, dielectric

I. Introduction

Relaxor ferroelectrics, a class of PbO-based complex perovskites, have evolved as a major field of study as promising high dielectric materials in the past few years. They offer advantages such as higher relative permittivity, lower sintering temperature, smaller intrinsic temperature dependence of permittivity and lower electric-field dependence of dielectric properties over traditional BaTiO_3 -based materials.¹ Relaxor ferroelectrics are typified by lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), which has been extensively investigated due to its wide application in multilayer capacitors (MLC) and actuators. However, the processing of PMN powders is complicated by the formation of stable and parasitic lead-niobate-based pyrochlore phases which lead to a drastic decrease in relative permittivity.² Much research has been carried out on the investigation of causes for the formation of pyrochlores in order to fabricate a pyrochlore-free PMN. In an attempt to achieve this, a number of wet chemistry-based synthesis routes have recently been engineered, including coprecipitation,³ sol-gel,^{4,5} citrate route,^{6,7} molten salt synthesis,⁸ partial oxalate method⁹ and hydrothermal synthesis.¹⁰ Almost all these solution routes are aimed at achieving a fine particle size and homogeneous mixing of the constituent components in order to enhance the formation of perovskite phase.

The preparation of ultrafine particles has been one of the pursued goals in many industries. A refinement in particle size is especially relevant to the perovskite family, as their electro-properties are strongly dependent on the crystallite size.^{11,12} However, it is difficult to obtain small and mono-dispersed particles by conventional methods because many particles sinter easily during the reaction of their precursor species. Such a problem can be alleviated by using micro-

emulsions as a media for chemical reactions. Microemulsions are thermodynamically stable mixtures of oil, water and surfactant/co-surfactant.¹³ Micro-emulsions form spontaneously when the constituent components are mixed together in an appropriate ratio. In microemulsion processing, aqueous domains act as "nanoreactors" for the precipitation/coprecipitation reactions, leading to the formation of nanosized precursor particles.¹⁴ Several electroceramic materials, including LaNiO_3 , La_2CuO_4 , BaPbO_3 , BaTiO_3 and SrZrO_3 have been successfully synthesized from microemulsions.^{15,16}

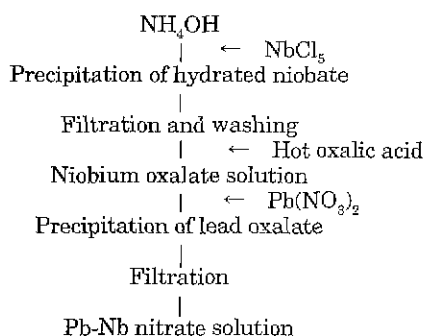
In this study, ultrafine PMN powders were synthesized from an inverse microemulsion consisting of cyclohexane, mixed poly(oxyethylene)₆ nonyl phenol ether (NP5) and poly(oxyethylene)₉ nonyl phenol ether (NP9), together with an aqueous phase. Hydroxide precursors were coprecipitated from nitrate solutions dispersed in the microemulsion by stepwise hydrolysis using aqueous ammonia solution as the precipitant. Ultrafine PMN powders of monophasic perovskite phase were subsequently obtained by calcining the microemulsion-derived precursor.

II. Experimental Procedure

1. Preparation of aqueous solution

It had been reported that a one-step coprecipitation of a PMN solution using ammonia solution as the precipitant was not suitable due to the loss of magnesium hydroxide during coprecipitation.^{3,17} Hence the stepwise precipitation procedure devised by Yoshikawa and Uchino¹⁷ was adopted and applied to the microemulsion systems in the present work. An aqueous solution containing a mixture of Nb^{5+} and Pb^{2+} ions and a separate aqueous solution containing Mg^{2+} ions were first prepared.

Niobium pentachloride, NbCl_5 (Fluka 99.9%), was added to



Scheme 1. Flow chart for the preparation of lead-niobium nitrate solution.

an excess amount of 2M NH_4OH solution to form hydrated niobate ($\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$), which was subsequently filtered and washed repeatedly until tested free of chloride ions using silver nitrate solution. The freshly precipitated niobate hydrate was dissolved in 1M hot oxalic acid ($\sim 80^\circ\text{C}$) to produce a niobium oxalate solution.¹⁸⁾ The amount of niobium content in the hydrated niobate precipitate was determined by thermogravimetric analysis based on niobium oxide (Nb_2O_5) as the final form.

With the subsequent addition of lead nitrate solution to the niobium oxalate solution, white gels of lead oxalate, $\text{Pb}(\text{C}_2\text{O}_4)$, was immediately precipitated. Hence a precalculated amount of lead nitrate $\text{Pb}(\text{NO}_3)_2$ (Merck >99%) dissolved in distilled water was added to the niobium oxalate solution to fully precipitate the oxalate ions as lead oxalate and with the required amount of lead ions remaining in the solution. A lead-niobium nitrate solution was thus obtained after lead oxalate was filtered off. On the other hand, a magnesium nitrate solution was separately prepared by dissolving an appropriate amount of hydrated magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fisons 99.0-101.0 %) in distilled water. A flow chart for the described preparation of lead-niobium nitrate solution is shown in reaction scheme 1.

2. Preparation of microemulsions

A ternary phase diagram for the microemulsion system consisting of cyclohexane (J.T.Baker, USA) as the oil phase, mixed poly(oxyethylene)₅ nonyl phenol ether (NP5) and poly(oxyethylene)₉ nonyl phenol ether (NP9) (NP5: NP9 weight ratio: 3:1, Albright and Wilson Asia Pte Ltd, Singapore) as the non-ionic surfactant and the aqueous phase of lead-niobium nitrate was first established. This was done by systematically titrating the aqueous phase into a given oil-surfactant mixture. The water-clear appearance of the mixture upon vigorous stirring indicated the formation of a microemulsion, while the compositions at each point of clear-turbid transitions were recorded. Thus, the boundary between the microemulsion region and turbid region in the ternary system was determined by repeating the same procedure to a series of oil-surfactant mixtures. Fig. 1a and 1b show the resulting microemulsion phase diagrams.

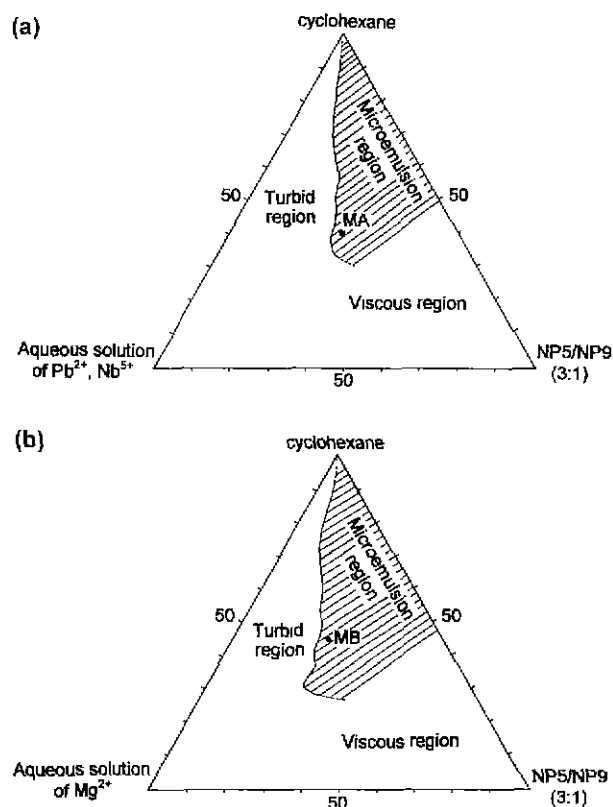
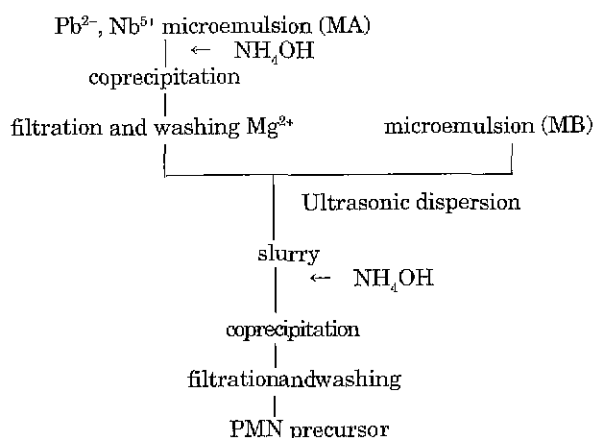


Fig. 1. (a) Ternary phase diagram at 25 °C for the system consisting aqueous solution of Pb^{2+} , Nb^{5+} nitrate solution, cyclohexane and NP5/NP9 (3:1). (b) Ternary phase diagram at 25 °C for the system consisting aqueous solution of Mg^{2+} nitrate solution, cyclohexane and NP5/NP9 (3:1).

The composition of 40 wt% cyclohexane, 30 wt% surfactant and 30 wt% aqueous phase of lead-niobium nitrate (designated MA), which is within the microemulsion region was chosen for coprecipitating lead and niobium hydroxides. A phase diagram for the ternary system containing magnesium nitrate solution as the aqueous phase in mixed cyclohexane and NP5+NP9 was established by following the same experimental procedure. On the other hand, microemulsion consisting of 45 wt% cyclohexane, 25 wt% surfactant and 30 wt% aqueous phase of magnesium nitrate (designated MB) was chosen for precipitating magnesium hydroxide together with the pre-prepared lead and niobium hydroxide precipitates from MA. The compositions of the two microemulsions and the concentrations of Pb^{2+} , Nb^{5+} and Mg^{2+} in the respective aqueous phases are given in Table 1. A flow chart for the preparation of the PMN precursor is shown in reaction scheme 2.

A sufficient amount of 2M ammonia aqueous solution was added dropwise to composition MA with vigorous stirring to coprecipitate lead and niobium hydroxides and the resulting precipitates were retrieved by filtration, followed by repeated washing using ethanol. The precipitates were then added to composition MB to form a slurry which was ultrasonically treated for about 20 minutes. A calculated amount of 2M aqueous ammonia solution was subse-



Scheme 2. Flow chart for the preparation of PMN precursor.

Table 1. Compositions of Inverse Microemulsions

Microemulsion	Weight % of each phase			Concentration of metal ions in aqueous phase
	Aqueous Solution	NP5/NP9	cyclohexane	
MA	30	30	40	0.084 M Pb ²⁺ 0.056 M Nb ⁵⁺ 0.5 M Mg ²⁺
MB	30	25	45	

quently added to the slurry with vigorous stirring to precipitate magnesium cations. The resulting precipitates were filtered and washed repeatedly with ethanol to remove the surfactant and oil phases and then dried at $\sim 80^\circ\text{C}$ in an oven for 12h.

3. Precursor and powder characterization

The PMN precursor obtained was characterized using thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) (Dupont 2100 thermal analyser) heated at a rate of $10^\circ\text{C}/\text{min}$ in air from room temperature to 900°C for both analyses. The precursor was calcined at 500°C for 2h to remove organic residuals before annealing at a high temperature ranging from 600 to 900°C for 2h each in an alumina crucible with cover. Organic content in the precursor and calcined PMN powders was examined using a Fourier-Transform Infra-Red (FTIR) spectroscopy (Bio-Rad FTS 135) over the range of 400 – 4000 cm^{-1} . Phase identification in the calcined PMN powders was carried out using a X-ray diffractometer (XRD, CuK α , Philips PW1729). Specific surface area of powders was measured using a Quantachrome BET surface analyzer (NOVA 2000). Morphology of powders was characterized using transmission electron microscope (TEM) (JOEL-100CX).

III. Results and Discussion

Fig. 1a and 1b show the ternary phase diagrams established at room temperature for the systems containing an aqueous solution of Pb-Nb-nitrates and Mg-nitrate, respec-

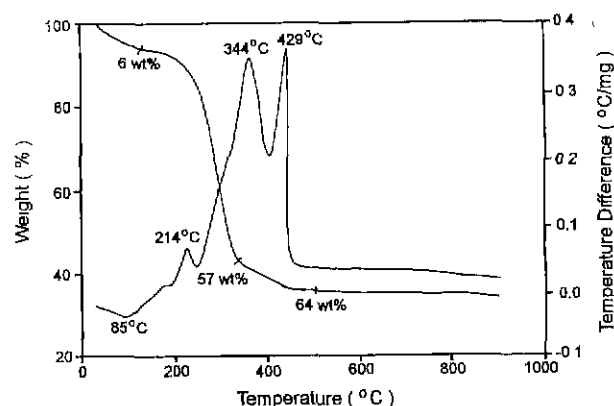


Fig. 2. TGA and DTA of microemulsion-derived PMN precursor ramped at $10^\circ\text{C}/\text{min}$.

tively, cyclohexane as the oil phase and NP5+NP9 (3:1 weight ratio) as the non-ionic surfactant. The shaded area refers to the microemulsion region in which the aqueous droplets are in the range of 5 to 30 nm ,¹⁹⁾ and therefore they are optically transparent. The NP5:NP9 weight ratio was controlled at 3:1, because our earlier experimental results showed that it produced the largest microemulsion region among various NP5:NP9 ratios. In both ternary systems, the transparent microemulsion region widens with increasing surfactant to oil phase ratio and the surfactant-rich compositions are very viscous. Having established the phase relationships in the two ternary systems, compositions MA and MB in Fig. 1a and 1b, respectively, are chosen for the preparation of PMN precursor as detailed earlier.

Results of the thermal gravimetric analysis (TGA) alongside with differential thermal analysis (DTA) of the as dried precursor are shown in Fig. 2. As observed from the TGA curve, there are three major weight losses. The first major weight loss of $\sim 6\%$ from room temperature to $\sim 150^\circ\text{C}$ is attributed to the desorption of physisorbed water and the elimination of oil and surfactant residuals from the precursor. This is supported by a small but broad endothermic reaction peak at $\sim 85^\circ\text{C}$ which spreads over the same temperature range. A drastic weight loss occurs over the temperature range of ~ 200 – 320°C which constitutes the second major weight loss of $\sim 50\%$ followed by a smaller weight loss up to $\sim 450^\circ\text{C}$. The observed weight loss from 200 – 450°C on the TGA curve is manifested as three sharp exothermic peaks on the DTA curve over the same temperature range. These exotherms are considered to be due to the dehydration of the hydroxide precursor to oxide together with the combustion of organic residuals from the precursor. A stable weight is attained for the precursor at $\sim 450^\circ\text{C}$ after a total weight loss of $\sim 64\%$. Furthermore, no peaks are observed on the DTA curve after 450°C .

To monitor the elimination of residual oil and surfactant phases from the microemulsion-derived PMN precursor with increasing temperature, spectroscopic analysis using FTIR was conducted on the as-dried powders and those cal-

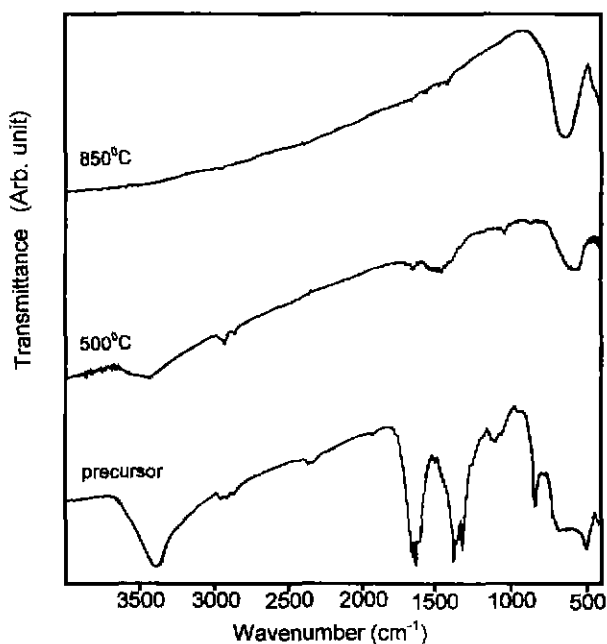


Fig. 3. FTIR spectra of PMN precursor and powders calcined at 500 °C and 850 °C for 2h each.

calcined at higher temperature of 500 °C and 850 °C for 2h each. As shown in Fig. 3, the presence of organic residuals in the as-dried precursor is indicated by the two sharp bands over the wavenumber range of 1300-1400 cm^{-1} and 1600-1700 cm^{-1} , which correspond to C-O and C=C stretching vibrations, respectively. These functional groups were not completely eliminated when the precursor was repeatedly washed and subsequently dried at 80 °C. As expected, the hydroxide nature of the as-dried PMN precursor was indicated by a relatively broad but strong vibrational band over the range of 3200-3700 cm^{-1} . Upon calcination at 500 °C, at which organic residuals should have been combusted and precursor attained stable weight on the TGA curve (Fig. 2), the band intensities relating to both hydroxyl and organic groups are reduced drastically although they are still visible. They disappear completely from the FTIR spectrum only when the precursor was calcined at 850 °C at which the only visible band over the range of 500-900 cm^{-1} corresponds to metal-oxygen bonds.

Fig. 4 shows the XRD traces for the PMN powders calcined for 2h at various temperature ranging from 600 to 900 °C. The amount of perovskite phase present in each powder was estimated using the following equation as suggested by Swartz and ShROUT,²⁰ on the basis of relative intensities of the major reflections for the pyrochlore and perovskite phases, respectively:

$$\% \text{ perovskite phase} = \frac{I_{\text{pyro}}}{(I_{\text{pyro}} + I_{\text{PMN}})} \times 100$$

where I_{pyro} refers to the intensity of pyrochlore (222) peak and I_{PMN} the intensity of perovskite (110) peak. A mixture of pyrochlore and perovskite phases are observed after cal-

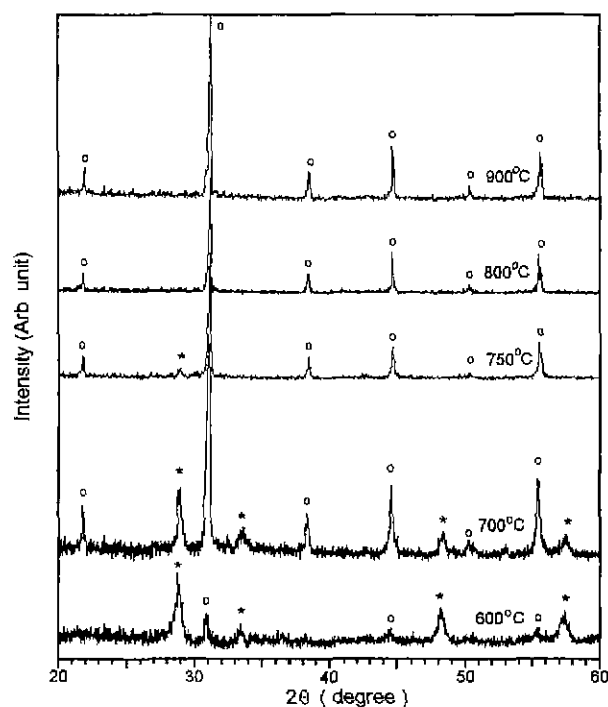


Fig. 4. XRD traces of microemulsion-derived PMN powders after calcination at different temperatures for 2h each. (O and * represent perovskite and pyrochlore phases respectively).

calcination at 600 °C. However, with increasing calcination temperature, percentage of perovskite phase increases at the expense of the pyrochlore phase, reaching 100% at 800 °C. The formation temperature for perovskite phase in the microemulsion-derived PMN precursor is compared favourably to those in the precursors prepared via conventional solid state reaction of mixed oxides.²¹ For that conventional method, a calcination temperature of 900 °C is required in order to obtain 95% perovskite phase in the mixed oxides with an addition of 5-20 mol % excess PbO and MgO. However, the dielectric properties often are adversely affected by these stoichiometry changes.²² The Columbite process²⁰ is effective in synthesizing a stoichiometric PMN perovskite phase from mixed oxides. However, it requires pre-reacting Nb_2O_5 and MgO to form MgNb_2O_6 by calcination at 1000 °C or above. In this study, we have shown that without going through the two stage solid state reactions and without adding excess PbO or MgO, PMN powders of 100% perovskite phase can be obtained successfully at a temperature as low as 800 °C. The apparent favourable factor in facilitating the formation of pure perovskite phase at a lowered temperature could be the refinement in compositional homogeneity and mixing scale as the co-precipitation was carried out in the nanosized domains of a microemulsion.

Specific surface area of the as-dried PMN precursor was measured to be 54 m^2/g which is equivalent to an estimated average particle size of 14nm. TEM micrograph of as-dried precursor as depicted in Fig. 5 shows agglomerates which are made up of smaller particles in the size range of

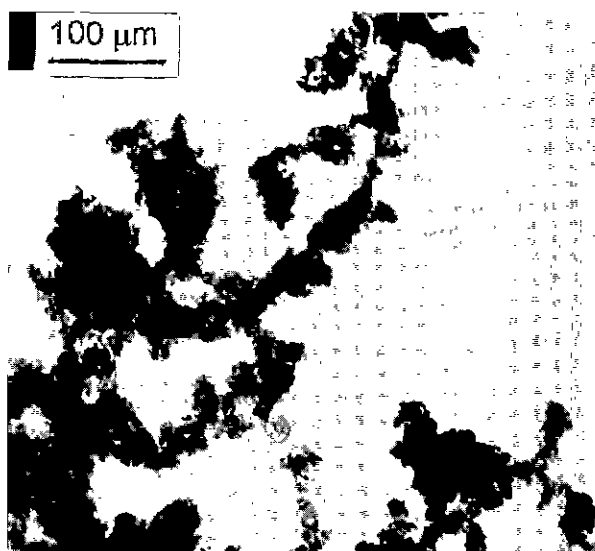


Fig. 5. TEM micrograph of microemulsion-derived PMN precursor.

~10nm. After calcination at 800 °C for 2h, specific surface area of powders was 8m²/g corresponding to an average particle size of 92 nm.

IV. Conclusions

Perovskite lead magnesium niobate $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) has been successfully prepared from an inverse microemulsion system consisting of cyclohexane, NP5+NP9 and an aqueous phase containing mixed lead and niobium nitrates and magnesium nitrate, respectively. By stepwise hydrolysis using an aqueous ammonia solution as the precipitant, PMN hydroxide precursor was obtained from the nitrate solution dispersed in the nanosized aqueous domains of these microemulsions. Monophasic PMN of perovskite phase was formed when the microemulsion-derived precursor was calcined at 800 °C. The resulting powders were ultrafine with an average particle size of ~92 nm as calculated from BET surface area of 8 m²/g.

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