JOURNAL OF MATERIALS SCIENCE 25 (1990) 5007–5013

Sol–gel processing and properties of lead magnesium niobate powders and thin layers

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Lead magnesium niobate powders and thin layers were formed from an alkoxide-based solution by sol–gel methods. The solution was synthesized by reacting a magnesium–niobium alkoxide solution with a lead acetate-based precursor solution. The effects of gelation conditions on the properties of the dried gel, and on the organic decomposition behaviour and crystalline phase development in gel-derived powders are reported. Gels prepared with greater molar ratios of water to alkoxide (3:1) had the largest surface areas (130 $m^2 g^{-1}$) and required the lowest temperature (320° C) for organic removal. The perovskite phase first appeared at temperatures near 700° C, and developed at a faster rate in gels prepared with higher water contents. Approximately 95% developed after 1 h at 700° C, or 5 min at 775° C. Dielectric thin layers were prepared on platinum-coated silicon substrates by a multilayered spin-casting method. The perovskite phase formed most readily in the thin layers by a fast-firing treatment at 800° C. Microstructures and electrical properties are reported for the integrated thin layer dielectrics. Ferroelectric hysteresis loops were observed.

1. Introduction

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), is a relaxor ferroelectric with important dielectric and electrostrictive properties [1, 2]. Among the assets of PMN are a high dielectric constant, a relatively low sintering temperature and a diffuse phase transformation. Consequently, PMN is under investigation as a material for actuator and capacitor applications, both in bulk and layered form. Also of interest is the application of relaxor-based dielectric thin layers on semiconductors, for possible use in dynamic random access memory (DRAM) elements and as integrated capacitors. In the present study we report the sol–gel processing of PMN, for the preparation of powders suitable for bulk applications, and for the spin-casting of thin-layer capacitors.

The processing of PMN ceramics with the desired perovskite structure has posed a considerable technological challenge. Solid state reactions of constituent oxides lead initially to the appearance of a cubic pyrochlore phase ($Pb_3Nb_4O_{13}$) which must be reacted further to form the perovskite phase [3]. The conversion reaction is usually incomplete, and any residual low dielectric constant pyrochlore phase dilutes the final electric properties. Pyrochlore-free PMN may be obtained by a solid state reaction of $MgNb_2O_6$ with PbO [3] or through the use of excess MgO or PbO [4]. Additionally, formation of the desired perovskite structure, $A(B'B'')O_3$, has been linked to the reactivity of the B′ site cation (i.e. Mg) [5]. Alternative chemical processing methods, such as sol–gel, may offer the homogeneity required to form the perovskite phase without stoichiometric variations.

Sol–gel is a versatile chemical processing method well suited for the formation of the fine powders and thin-layered ceramics. Homogeneity can be achieved through intimate mixing in solution, and the resulting gel-derived powders are usually fine and reactive. As a result, lower temperature phase formation is possible. The sol–gel route involves the preparation of an alkoxide-based solution by mixing or reacting metal alkoxides and inorganic salts in a common solvent. The regulated addition of water results in hydrolysis and condensation reactions which create a rigid polymeric gel, or, when lesser amounts of water are used, a stable solution for spin-casting thin layers. Additionally, studies of silicate [6–9] and $PbTiO_3$ [10, 11] alkoxide systems have shown that gel structure and the physical characteristics for dried gels (e.g. pore size, surface area, free volume, etc.) are determined by the choice of gelation conditions (i.e. water to alkoxide ratio, acid or base addition, etc.). Structural variations in the gel may play an important role in subsequent crystallization behaviour.

This study focuses on (i) the development of a solution system for PMN, (ii) formation of gels and powders, and (iii) the determination of gelation and heat-treatment conditions necessary for perovskite phase development in gel-derived powders. Additionally, the processing and properties of PMN thin layers formed by spin-casting on platinized silicon were investigated.

2. Experimental procedure

2.1. Solution preparation

A flow diagram for the preparation of a 1 M PMN solution is given in Fig. 1. All solutions were prepared using Schlenk apparatus under dry nitrogen or vacuum

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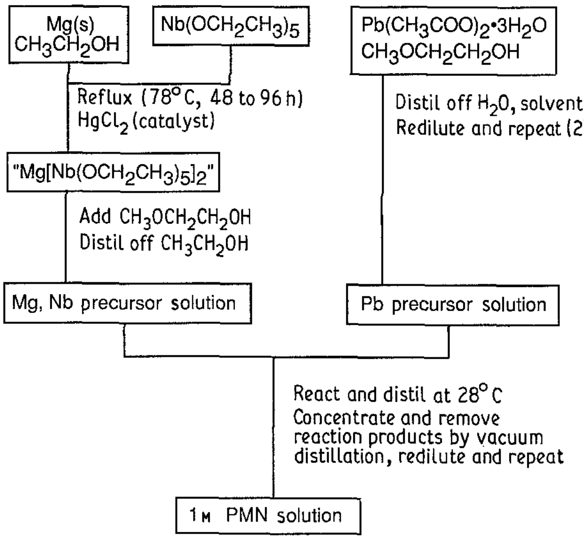

Figure 1 Flow diagram for the preparation of PMN solution.

conditions as required. Lead acetate trihydrate (> 99%, Aldrich), $Pb(CH_3COO)_2 \cdot 3H_2O$, was dissolved in 2-methoxyethanol (> 99%, HPLC grade, Aldrich), $CH_3OCH_2CH_2OH$, and heated. The solution was distilled until the temperature of the condensing vapours reached ~ 124° C, the boiling point of 2-methoxyethanol. Two additional dilutions and distillations were carried out to complete the dehydration. The lead precursor solution was concentrated to approximately 2 M during the final distillation step and was ready for combination with a magnesium-niobium precursor solution.

The magnesium–niobium precursor solution was synthesized by a method similar to that given by Goel *et al.* [12]. Fine magnesium powder (> 99%, − 50 mesh, Aldrich) was combined with dry ethanol (dried using standard procedures [13]) in a three-neck flask equipped with a reflux condenser. Niobium ethoxide, $Nb(OCH_3CH_2)_5$, prepared from $NbCl_5$ by the ammonia method [14], was then added to the vessel via a cannula, and the mixture was refluxed at 78° C for 48 to 96 h. The reaction was aided by the addition of a small amount of catalyst, $HgCl_2$ (ACS grade, Fisher). At this stage, a typical solution contained 60 ml CH_3CH_2OH, 5.304 g (16.7 mmol) $Nb(OCH_2CH_3)_5$, 0.2056 g (8.33 mmol) Mg and 0.01 g (0.037 mmol) $HgCl_2$. Goel *et al.* reported the formation of a magnesium niobium double alkoxide by the following reaction

$$\begin{aligned} Mg(s) + 2Nb(OCH_2CH_3)_5 + 2CH_3CH_2OH \\ \rightarrow Mg[Nb(OCH_2CH_3)_6]_2 + H_2(g)\uparrow \qquad (1) \end{aligned}$$

The double alkoxide was not isolated and characterized in the present study. Instead, an "$Mg[Nb(OCH_2CH_3)_6]_2$" solution was prepared, refluxed with excess 2-methoxyethanol for 1 h and distilled to form a magnesium–niobium precursor solution.

The two precursor solutions (i.e. lead- and magnesium–niobium) were mixed at room temperature, reacted at 128° C and concentrated by distillation. Three successive dilutions and vacuum distillations were used to remove the by-products (primarily methoxyethyl acetate) and create a stable solution. The volume of the final solution was then adjusted to give a 1 M PMN stock solution.

2.2. Gel and thin-layer formation

For the preparation of bulk gels, the 1 M PMN solution was combined with an equal volume of a 2-methoxyethanol hydrolysis solution which contained a specific concentration of water (2 or 3 M) and additive (0.2 M NH_4OH or 0.2 M HNO_3). The procedure resulted in transparent 0.5 M PMN gels which contained either 2 or 3 mol water per mol PMN. In this study, gels were designated by the additive type (acid or base) and the relative concentration of water used in gelation (2 or 3). For example, A2 denotes a gel prepared with an acid additive and 2 mol water per mol PMN. Gels were dried at 140° C for 12 h, crushed in a mortar and pestle and converted to ceramic powder by fast-firing treatments in air. Samples were placed in a preheated tube furnace for 5 to 60 min and quenched to room temperature.

Thin layers were deposited on platinum-coated silicon substrates by a spin-casting method. Substrates were first degreased with trichlorethylene, and rinsed in acetone and isopropanol. A solution for spin-casting was prepared by mixing equal volumes of (i) 1 M PMN solution, (ii) 2-methoxyethanol and (iii) a 2-methoxyethanol hydrolysis solution (1 M water and 0.1 M NH_4OH). After ageing for approximately 48 h, the partially hydrolysed solution was syringed through 0.4 μm filters on to the substrates which were then spin-cast at 2100 r.p.m. for 50 sec. Each layer of solution was annealed at ~ 270° C on a hot plate for 30 sec. The deposition and annealing procedures were repeated two to six times to increase the thickness, and the final multilayer form was fast-fired at 800° C for 5 mins.

2.3. Characterization

The physical properties of dried gels, the organic decomposition behaviour and the crystalline phase development for gel-derived powders were investigated. Surface area and powder density were determined by BET analysis and helium gas pycnometry, respectively, for lightly crushed, dried gel powders. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) for gel-derived powders were determined in air at 10° C min^{-1}. The results were used in conjunction with X-ray diffraction (XRD) for heat-treated powder to determine crystalline phase development as a function of temperature. The relative amounts of perovskite and pyrochlore phases were estimated by comparison of peak heights of the most intense diffraction lines, according to

$$\%\ \text{perovskite} = \frac{I(1\,1\,0)_{\text{per}}}{I(1\,1\,0)_{\text{per}} + I(2\,2\,2)_{\text{pyro}}} \times 100 \qquad (2)$$

Microstructures and properties for thin-layer dielectrics were investigated. Grain size and layer thickness were determined by scanning electron microsopy (SEM), and XRD was used to monitor crystalline phase development. Thin-layer capacitors were fabricated by sputtering an array of square gold electrodes ($3.6 \times 10^{-4}\,cm^2$) on the film surface. The bottom electrode (platinum layer) and the top gold electrode were contacted by micropositioners to a HP 4192A impedance analyser. The electric-field dependence of polarization was observed on a modified Sawyer–Tower bridge.

3. Results and discussion
3.1. Gel-derived powders
3.1.1. Gelation and dried gel properties
The number of moles of water, per mole of PMN, used in gel formation was observed to affect gelation characteristics. Transparent gels were formed by combining equal volumes of the 1 M PMN stock solution with certain hydrolysis solutions (2 or 3 M water). Larger concentrations of water (> 3 M) yielded rapid gelation and incomplete mixing of alkoxide and hydrolysis solutions. Lesser concentrations of water resulted in stable solutions or long gelation times. Gelation in alkoxide-based systems is due to hydrolysis and condensation reactions [8]. Addition of water to an alkoxide solution results in hydrolysis according to the generic reaction.

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + ROH \quad (3)$$

Partially hydrolysed species condense with OR or OH groups on other species, leading to metal–oxygen–metal bonds and the evolution of a three-dimensional gel network. The structure of the polymeric gel network has been found to depend on gelation conditions for many systems, as will be discussed shortly. During drying, solvent which is interspersed within the gel network evaporates, and the gel shrinks, undergoing further condensation and rearrangement. The gels prepared in this study exhibited phase separation (i.e. a liquid was expelled from the collapsing gel during drying). B3 and A3 exhibited the greatest amount of phase separation, and A2 the least. This phenomenon has been observed in many organic and inorganic polymer systems, and has been correlated with gel structure. For example, phase separation is more common in highly cross-linked gels in the silicon alkoxide system [7].

Surface area and powder density are reported in Table I for dried gel powders. The surface area was higher for gels prepared with 3 mol water per mol PMN (A3, B3) and greater in basic gels of an equivalent water concentration. Differences in powder density among the gels were not as significant, but for a given additive type, density was found to be greater for gels prepared with a larger water to PMN ratio. A gel structure having both high surface area and powder density might consist of locally dense regions surrounded by a large amount of open porosity (not accounted for in the pycnometer method). By contrast, low-density low surface area gels might have a larger pore size and contain closed porosity. The results in Table I are consistent with those reported by Schwartz *et al.* for lead titanate gels [10] and may be related to changes in gel structure. In the silicon alkoxide system, for example, Brinker reported that gels with large water to alkoxide ratios consisted of highly cross-linked clusters linked together at many branch points, while those prepared with lower water to alkoxide ratios were more weakly cross-linked with a linear-type polymer structure [6]. Additions of base were found to have an effect similar to high water concentrations and promoted cross-linking, whereas acid additions promoted the formation of a more linear-type polymer. During drying, linear-type gels can undergo rearrangement more readily and consequently have less open porosity. Cross-linked gels will tend to maintain a more open branched structure of clusters. In this study the highest surface areas were obtained for large water to PMN ratios (B3, A3), indicating that these gels had more open, cross-linked structures than gels prepared with lesser amounts of water. Additionally, for a given water concentration, basic gels had a larger surface area than their acidic counterparts. The gel structure may also have an effect on crystalline phase formation.

TABLE I Dried gel properties

Gel	Surface area ($m^2 g^{-1}$)	Powder density ($g cm^{-2}$)
A2	1.3	4.8
A3	77	5.1
B2	66	5.2
B3	130	5.3

3.1.2. Organic decomposition
Fig. 2 illustrates TGA and DTA characteristics for dried gels B2 and B3. The gel prepared with less water (B2) lost weight in several stages, finally completing organic burn-out around 500° C. A step-wise weight loss was also noted for lead titanate gels prepared

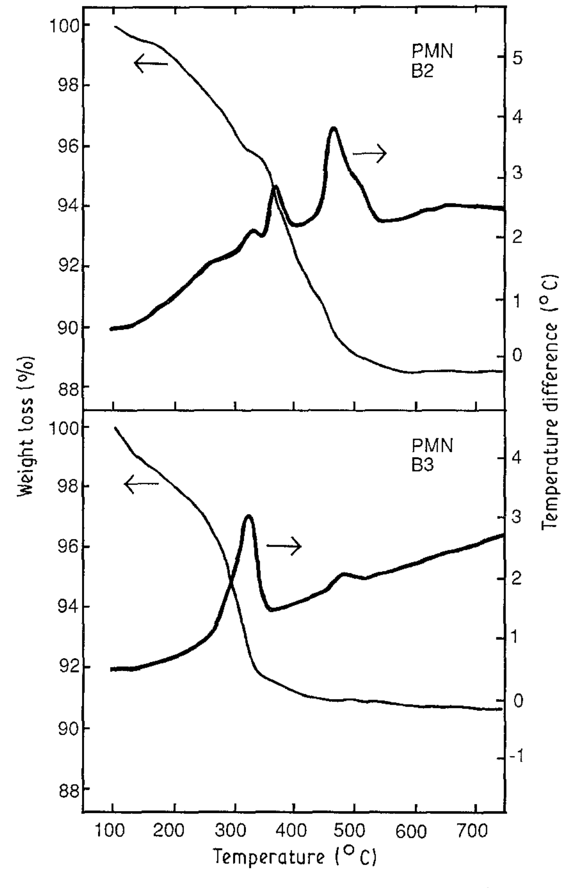

Figure 2 The effect of gelation conditions on the organic decomposition behaviour and crystallization of gel-derived powders.

under similar hydrolysis conditions, and was attributed to variations in bonding of organic groups in the gel network and/or the presence of several different types of organic groups [10]. By contrast, gels prepared with a larger amount of water (B3) were characterized by a single weight loss step which was complete by 320° C. That is, the organic burn-out temperature was significantly reduced. The total organic content of B3 after drying was 9% by weight, while that of B2 was slightly greater (11%). Gelation with a greater quantity of water most likely leads to increased hydrolysis and the removal of a greater fraction of organic material as alcohol in the drying step. Acidic gels pyrolysed similarly, with A2 and A3 exhibiting step-wise and single-step weight losses, respectively. Acidic gels contained more organic material after drying (15% for A2 and 11% for A3).

Gelation conditions also affect crystallization behaviour. DTA data in Fig. 2 give exotherms for each stage of weight loss by organic pyrolysis, with additional peaks for the crystallization of material. For B2, three exotherms at approximately 250, 360 and 460° C were associated with pyrolysis of organics, while the small exotherm at ~320° C occurred in a region of little weight loss, and was probably due to the formation of a crystalline phase. XRD revealed the transitory appearance of a crystalline lead phase at temperatures between 330 and 360° C in B2, and from 300 to 420° C in A2. The lead phase developed only in gels which had a gradual organic removal process (A2, B2); and formed at a lower temperature, and in greater amount, for the acidic gel. Based on surface area data and comparisons with other alkoxide systems, gels prepared with lower concentrations of water were believed to consist of weakly cross-linked structures. Thus, the appearance of crystalline lead during organic decomposition of gels of low water concentration suggests the presence of weakly bound lead-containing species. Given that the PMN solution was prepared by reacting a magnesium–niobium alkoxide solution with a lead acetate-based solution, the presence of bridging acetate groups is a distinct possibility. Loosely bound organics could possibly be removed at lower temperatures leaving unbound lead. The local reducing environment accompanying organic burn-out may have allowed for the retention of lead in metallic form rather than as the oxide. Upon completion of organic decomposition and the concurrent crystallization of pyrochlore (~460° C), only the pyrochlore phase could be detected by X-rays. The lead was most likely well dispersed and combined with the remainder of the gel to form the pyrochlore phase.

By contrast, gels prepared with a greater amount of water (B3, A3) exhibited weight loss at lower temperatures and transformed directly from the amorphous to the pyrochlore state. As illustrated in Fig. 2, B3 had an exotherm at ~320° C for organic burn-out, and another at 470° C for crystallization to the pyrochlore phase. X-ray diffraction data confirmed that B3 and A3 both transformed directly from an organic-free amorphous state to a cubic pyrochlore phase and finally into the perovskite phase. Therefore, the use of a larger amount of water in gelation may be desired, in that a more cross-linked gel network is formed, and the homogeneity achieved in solution is retained in the gel and dried gel powder.

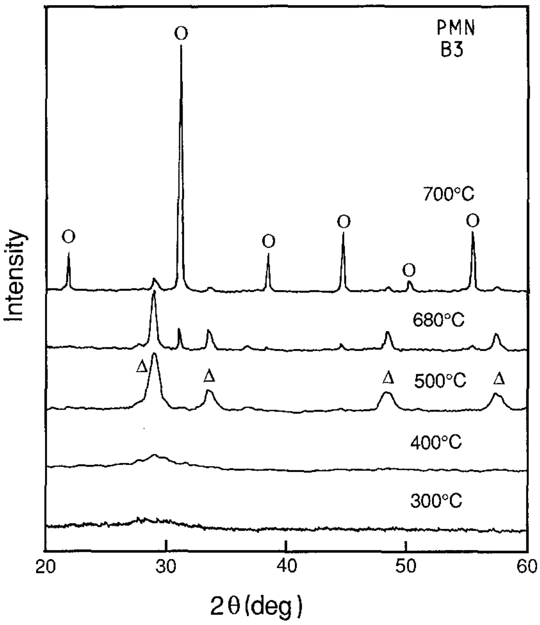

Figure 3 X-ray diffraction analysis of PMN gel-derived powder for 1 h heat-treatments: (○) perovskite, (△) pyrochlore.

3.1.3. Perovskite phase development

Fig. 3 illustrates the development of crystalline phases in B3 for 1 h heat-treatments at the temperatures given. As previously described, dried powders and those heated below ~450° C were amorphous, while higher temperature treatments resulted in the formation of a cubic pyrochlore phase. This pyrochlore was of the type described by other investigators [3] and formed in all gel-derived powders at temperatures around 450° C. The perovskite phase first appeared at 680° C, but did not form in abundance until 700° C. The phase development in the other gels was similar to that given for B3. Additionally, A2 and B2 formed a transitory lead phase, as discussed, and also contained a small amount of PbO phase between 650 and 680° C.

Development of the perovskite phase for B3 is given in Fig. 4. At 700° C the perovskite phase content increased gradually from 36% after 15 min to 92% after 1 h. A 20 h treatment at 700° C increased the phase content only slightly to ~95%. At slightly

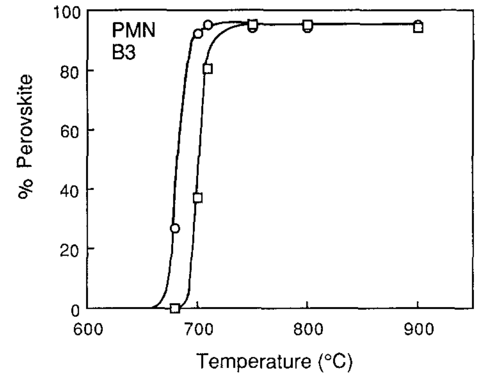

Figure 4 The effect of heat-treatment temperature and time on perovskite development: (○) 60 min, (□) 15 min.

higher temperatures, shorter times (e.g. 15 min at 750° C or 5 min at 775° C) were required for the formation of > 95% perovskite. Longer time (1 h) at higher temperatures did not lead to any significant increase in the perovskite phase content (~ 95%).

The rate of perovskite phase formation at temperatures near 700° C was dependent on gelation conditions. Data for the development of the perovskite phase with time at 710° C are given in Table II. The amount of perovskite phase increased more rapidly for gels prepared with higher water to PMN ratios (B3, A3). During the formation, B3 and A3 developed into the perovskite phase more rapidly, but eventually all gels reached a similar end-point value. The increased reactivity of these gels may possibly be linked to their proposed gel structures. Higher water concentrations give more cross-linked structures which retain better homogeneity throughout gelation, drying and organic decomposition, whereas those prepared with a lower water concentration, probably form less cross-linked structures which results in weakly bound lead species. The rate of reaction could have been slowed in B2 and A2 by the necessity for increased diffusion of segregated species to complete the reaction. Additionally, gel structure may have had an effect on reaction rate. Conditions of high water concentration with a base additive gave gels with larger surface areas, increasing the available surfaces for reaction.

The solution chemistry used in this study may also be responsible for the speed of perovskite phase development. Ravindranathan *et al.* prepared PMN from a sol–gel process using a 2-methoxyethanol system and $Mg(OCH_2CH_3)_2$, $Nb(OCH_2CH_3)_5$ and dehydrated $Pb(CH_3COO)_2 \cdot 3H_2O$ as starting materials [15]. They obtained ~98% perovskite for 120 and 2 h heat-treatments at 700 and 775° C, respectively. Data for shorter times were not reported. The faster rates of formation for the perovskite phase observed in the present investigation may be due to an increased association of B site cations obtained by the prereaction of magnesium metal and niobium ethoxide prior to the addition of the lead precursor solution. This procedure could be considered as a solution analogue to the solid state reaction process for precalcined $MgNb_2O_6$. Additionally, the different gelation and drying procedures used in the present study may have promoted perovskite formation. Again, recent chemical analyses (e.g. ICP, AA) indicate the possible presence of a small excess of lead (~ 2 to 4 mol %) which could influence the rate of perovskite formation [16]. In a recent report, a sol–gel procedure involving the formation of $Mg[Nb(OCH_2CH_3)_6]_2$, and combination with lead alkoxide, is described [16]. The results are in good agreement with the present investigation. An aerogel was formed by hypercritical drying (250° C, 63 bar*) and converted to ~ 100% perovskite PMN on heat-treatment at temperatures near 700° C. An aerogel should have a very porous, high surface area structure, similar to the proposed structure of the gels prepared from large water contents and base additions.

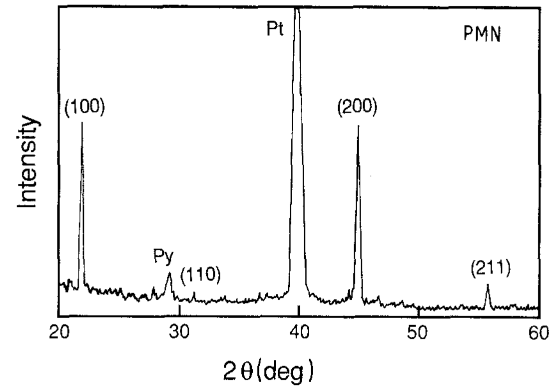

Figure 5 X-ray diffraction analysis of PMN thin layers spun-cast on platinum-coated silicon and fast-fired at 800° C for 5 min (perovskite is noted by (*h k l*) values).

3.2. Thin-layer processing and properties

Dielectric thin layers were deposited on platinum-coated silicon substrates by a spin-casting method. The as-deposited and annealed coatings were amorphous. On fast-firing at 800° C for 5 min, crack-free, crystalline layers were developed. Fig. 5 gives the XRD characteristics for the thin layers, illustrating a preferential orientation for the perovskite phase and only a small apparent amount of pyrochlore phase. The perovskite alignment prohibited the use of XRD methods to estimate the phase content. As demonstrated for gel-derived powders, perovskite phase content increased rapidly at temperatures near 800° C. Processing times were kept brief in order to avoid possible diffusion effects between the coating and the substrate. Thin layers prepared by fast-firing at lower temperatures or at slower heating rates were found to contain less perovskite. Perovskite orientation may be due to the growth of favourably oriented grains. The lattice parameter for platinum (a = 0.3923 nm) is close to perovskite (a = 0.404 nm) (i.e. within 3%). Stress and surface energy effects could also aid alignment.

Fig. 6 shows a scanning electron micrograph of the surface of a seven-layered coating (~0.21 μm thick) deposited on platinum-coated silicon and fast-fired at 800° C for 5 min. XRD data for this coating were given in Fig 5. The microstructure was characterized by a bimodal grain size distribution, containing larger and smaller sized grains, approximately 0.5 to 1.0 and 0.04 μm, respectively. SEM investigations of cross-sections revealed that the smaller grains were more prevalent on the surface and often covered larger grains. The frequency and size of larger grains

TABLE II Perovskite phase development with heat-treatment time at 710° C

Gel	Perovskite (%)			
	5 min	15 min	30 min	60 min
A2	0	51	78	90
A3	9	84	91	93
B2	0	64	89	92
B3	16	81	93	95

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*1 bar = 10^5 Pa.

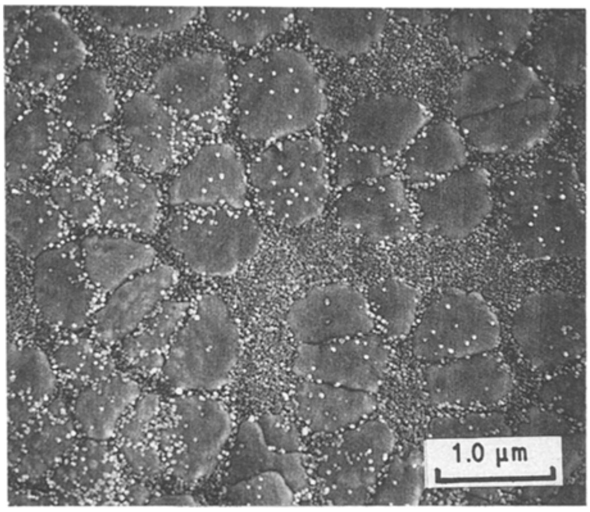

Figure 6 Scanning electron micrograph of the surface of PMN spun-cast on platinum-coated silicon and fast-fired at 800° C for 5 min.

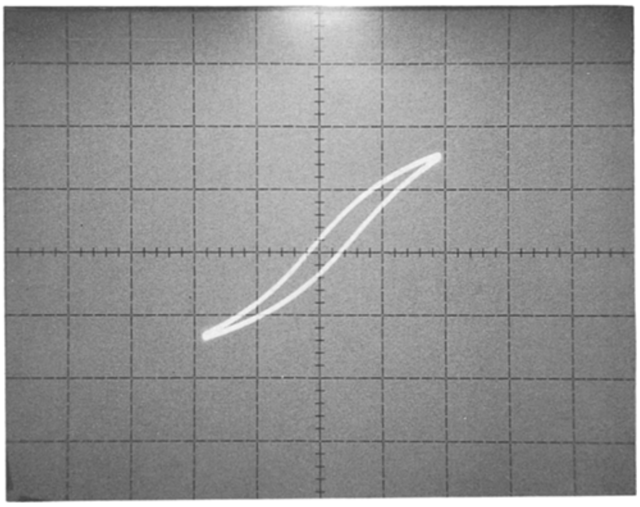

Figure 8 Slim loop polarization reversal for a PMN thin layer dielectric (50 Hz; x-axis: 1 division = 90 kV cm^{-1}; y-axis: 1 division = 14 μC cm^{-2}).

increased with film thickness, suggesting that the two grain sizes did not necessarily denote two distinct crystalline phases, but may be due to crystallization, grain growth and densification phenomena.

The frequency dependences of dielectric constant and loss tangent for PMN thin layers are given in Fig. 7 at two oscillation levels. The dielectric constant of thin layers was calculated to be 1000 to 1250 at room temperature, considerably less than the value for bulk polycrystalline PMN at room temperature (~ 10 000). The presence of residual pyrochlore, and additional factors such as grain size, stress and interfacial effects may be responsible for the lower dielectric constant, and are under investigation. The dielectric properties were dependent on the magnitude of the a.c. field. Although these measurements were made at a temperature greater than the average Curie temperature for PMN (– 15° C), the increase in dielectric constant with a.c. field may indicate the presence of residual polar microregions. This type of behaviour is typical of relaxor ferroelectrics which are characterized by diffuse phase transformations, in which properties such as spontaneous polarization decrease gradually over a span of temperatures rather than abruptly at the transition temperature. Further evidence of residual ferroelectricity was determined by polarization reversal measurements on thin layers. Slim hysteresis loops were observed at room temperature, as shown in Fig. 8. A spontaneous polarization of 6 μC cm^{-2} and a coercive field of 18 kV cm^{-1} were measured.

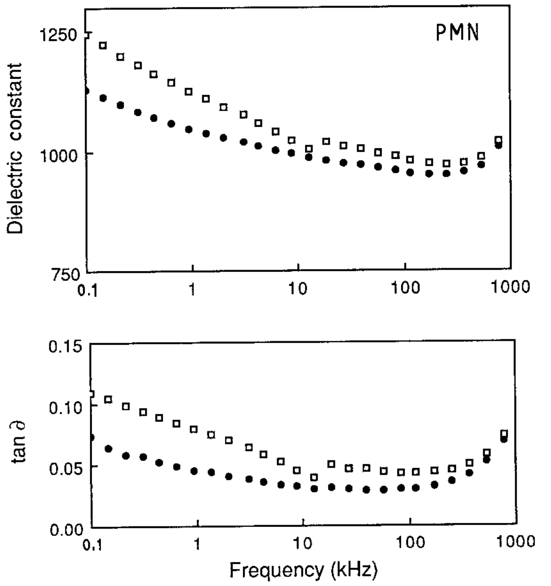

Figure 7 Dielectric constant and loss for a PMN thin-layer dielectric. (□) 36 kV cm^{-1}, (●) 12 kV cm^{-1}.

Work in progress is designed to give further understanding of the role of heat-treatment and additives on microstructure development and electrical properties of thin layer PMN devices, and will be reported in due course.

4. Conclusions

A solution system for PMN was developed and used to prepare ceramic powders from bulk gels and thin layers by a spin-casting method. The results of the investigation are as follows.

1. The surface area of dried gel powders was a function of the gelation conditions (i.e. the molar ratio of water : PMN, acid or base additions). Greater concentrations of water and the use of base additions were found to promote the formation of high surface area dried gels.

2. The gelation conditions also influenced the pyrolysis of organic content and the low-temperature crystallization behaviour of gel-derived powders. Gels prepared with lower water contents had a more gradual loss of organic content with temperature and formed a metastable crystalline lead phase during organic removal. Gels prepared with higher water concentrations decomposed in a single step, at a low temperature (320° C), to form organic-free amorphous powder, which then crystallized into pyrochlore (470° C) and finally formed perovskite (~ 700° C). Increased cross-linking in gels with the higher water

content was believed responsible for the observed behaviour.

3. The rate of pyrochlore to perovskite phase transformation in gel-derived powders was dependent on the heat-treatment temperature and gelation conditions. The perovskite phase formed very rapidly at temperatures slightly greater than 700° C, and the reaction rate was greatest for gels which had larger surface areas and were prepared with higher water concentrations.

4. Dielectric thin layers were formed on platinum-coated substrates. A large amount of perovskite phase developed under fast-firing conditions at 800° C. A dielectric constant of approximately 1100 was calculated, and the possible presence of polar microregions was noted from a.c. field dependences of dielectric constant and loss, and the observation of slim loop ferroelectric behaviour.

Acknowledgements

The authors gratefully acknowledge support from US DOE DMR-DE-ACO2-76ER01198. We thank Dr T. A. Bier for surface area measurements and the use of the Center of Electron Microscopy, University of Illinois, and R. W. Schwartz and D. J. Eichorst for their advice and helpful discussions.

References

1. S. L. SWARTZ, T. R. SHROUT, W. A. SCHULTZE and L. E. CROSS, *J. Amer. Ceram. Soc.* **67** (1984) 311.
2. S. NOMURA and K. UCHINO, *Ferroelectrics* **41** (1982) 117.
3. S. L. SWARTZ and T. R. SHROUT, *Mater. Res. Bull.* **17** (1982) 1245.
4. M. LEJEUNE and J. P. BOILOT, *ibid.* **20** (1985) 493.
5. *Idem, Ceram. Int.* **8** (1982) 99.
6. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER and C. S. ASHLEY, *J. Non-Cryst. Solids* **48** (1982) 47.
7. D. W. SCHAEFER and K. D. KEEFER, *Mater. Res. Soc. Symp. Proc.* **32** (1984) 1.
8. K. D. KEEFER, *ibid.* **32** (1984) 15.
9. B. E. YOLDAS, *J. Non-Cryst. Solids* **63** (1984) 145.
10. R. W. SCHWARTZ, D. A. PAYNE and A. J. HOLLAND, in "Ceramic Powder Processing Science" edited by H. Hausner, G. R. Messing and S.-I. Hirano (Deutsche Keramische Gesellschaft, 1989) p. 513.
11. Y. HAYASHI and J. B. BLUM, *J. Mater. Sci.* **22** (1978) 2655.
12. S. GOEL, A. B. GOEL and R. C. MEHROTRA, *Syn. React. Inorg. Metal-Org. Chem.* **6** (1976) 251.
13. D. D. PERRIN and W. L. F. ARMAREGO, "Purification of Laboratory Chemicals" (Pergamon Press, New York, 1988) p. 174.
14. D. C. BRADLEY, B. N. CHAKRAVAT and W. WARDLAW, *J. Chem. Soc.* (1956) 2831.
15. P. RAVINDRANATHAN, S. KOMARNENI, A. S. BHALLA, R. ROY and L. E. CROSS, *Ceram. Trans.* **1** (1987) 182.
16. F. CHAPUT, J. P. BOILOT, M. LEJEUNE, R. PAPIERNIK and L. G. HUBERT-PFALZGRAF, *J. Amer. Ceram. Soc.* **72** (1989) 1335.

Received 17 August
and accepted 1 November 1989