

The role of drying-control chemical additives on the preparation of sol-gel derived PLZT thin films

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Films of $\text{Pb}_{x/100}\text{La}_{x/100}(\text{Zr}_{y/100}\text{Ti}_{z/100})_{1-x/400}\text{O}_3$ with $x = 8$, $y = 65$ and $z = 35$ (PLZT(8/65/35)) with a single perovskite structural phase were successfully prepared by using drying-control chemical additives in sol-gel processing followed by rapid thermal annealing at 600 °C for only 1 min on Si(Pt) substrates. The roles of the drying-control chemical additives ethylene glycol and formamide in the gel preparation were studied. The hysteresis loop of PLZT(8/65/35) thin film was measured. The remanent polarization and coercive field were found to be about $1.3 \mu\text{C cm}^{-2}$ and 15 kV cm^{-1} , respectively.

1. Introduction

The solid-solution system lead-lanthanum-zirconate-titanate $\text{Pb}_{x/100}\text{La}_{x/100}(\text{Zr}_{y/100}\text{Ti}_{z/100})_{1-x/400}\text{O}_3$, described as PLZT($x/y/z$), has been widely investigated among ferroelectric ceramics due to their interesting ferroelectric, piezoelectric, pyroelectric and electro-optic properties [1–5]. The thin films are excellent candidates for many applications such as ferroelectric non-volatile memories, pyroelectric detectors, surface acoustic wave substrates, optical image storage devices, optical modulators, optical switches and optical display devices [5–9]. Thin films of PLZT have been prepared by r.f. sputtering [10–14] and sol-gel methods [15–17]. In recent years, the sol-gel processing method has attracted much interest for the fabrication of oxide films. Such chemical processing routes offer a number of advantages over conventional vacuum deposition. These include starting materials purity, better stoichiometric control and homogeneity, lower sintering temperature, an easier fabrication process and low cost.

Crack formation during the drying is one of the most serious problems in thin film fabrication via sol-gel processing. Capillary forces and local differential stresses have generally been attributed to drying stresses which cause crack formation. The capillary force depends on the ratio of liquor evaporation which is a function of solvent vapour pressure, and is inversely proportional to the pore size. The local differential stress stems from the non-uniform pore size distribution in the deposited film. The pore size and liquid vapour pressure can be controlled by adding a drying-control chemical additive (DCCA) to the mixed metal-alkoxide solution.

In this study, we investigate the role of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) and formamide (NH_2CHO)

when used as a DCCA in the low-temperature processing of sol-gel derived PLZT(8/65/35) thin films on platinum-coated silicon substrates. The crystal phase and P - E hysteresis loop of these films have also been studied.

2. Experimental procedure

For the preparation of PLZT(8/65/35) precursor solution, lead acetate hydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, lanthanum nitrate hydrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, zirconium n-tetrapropoxide $\text{Zr}(\text{OC}_3\text{H}_7)_4$ and titanium tetrabutoxide $\text{Ti}(\text{OC}_4\text{H}_9)_4$, were used as the starting materials. 2-methoxyethanol $\text{H}_3\text{COCH}_2\text{CH}_2\text{OH}$ was used as a solvent. Lanthanum nitrate hydrate replaced lanthanum acetate $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.5\text{H}_2\text{O}$ in order to prevent the common ion effect of CH_3COO^- ion which reduced the solubility of La^{3+} and Pb^{2+} ions. This effect of a common ion on solubility can be understood on the basis of Le Chatelier's principle.

The flow diagram for the preparation of the precursor solutions, gels and films is shown in Fig. 1. Lead acetate hydrate and lanthanum nitrate hydrate were first dissolved at 70 °C in 2-methoxyethanol and the solution was subsequently dehydrated at 120 °C. The dehydrated solution was cooled at 90 °C before zirconium n-tetrapropoxide was added. The solution was again refluxed to 120 °C and titanium tetrabutoxide was added; this solution was stirred until a clean solution was obtained. Ethylene glycol or formamide was added to the solution as DCCA; it was then aged to yield a gel.

The order of adding alkoxides to the metal-organic solution is very important. If titanium tetrabutoxide was added before zirconium n-tetrapropoxide, the solution became opaque. This may be due to titanium tetrabutoxide reacting with water and forming a white

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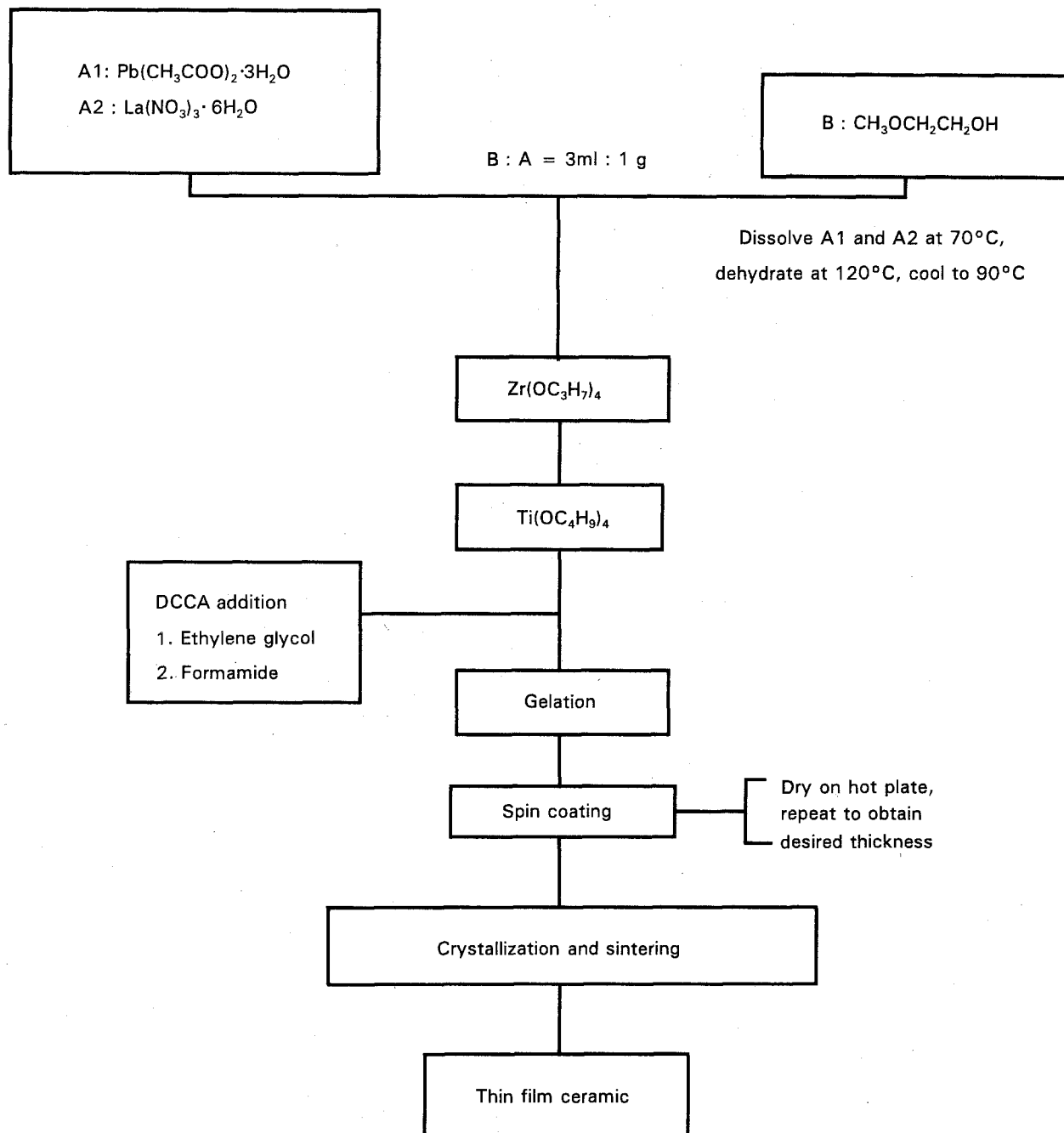


Figure 1 Flow chart of preparation of PLZT thin film by sol-gel processing.

precipitate of $\text{Ti}(\text{OH})_4$. The DCCA also plays an important role in determining the network of the resulting polymeric structure, lowering the sintering temperature and influencing the properties of the sintered film [18–25]. Platinum deposited on Si(100); Si(Pt), was used as substrate. Films were deposited by spin-coating solutions at 3500 r.p.m on substrates, then drying on a hotplate at about 300°C for 30 s to remove organic materials. Successive deposition of the film was repeated to obtain the desired thickness.

The pyrolysis of deposited films was analysed by thermogravimetric analysis (TGA) (Seiko TG/DTA 300) at a heating rate of $10^\circ\text{C min}^{-1}$ up to 650°C . The crystalline phase of the films was determined from powder X-ray diffraction patterns. The microstructure was observed by scanning electron microscopy (SEM) (Hitachi Model S-2500). Ferroelectric P - E hysteresis

loops of the films deposited on Si(Pt) substrates were measured by using a Sawyer-Tower circuit at a 1 kHz.

3. Results and discussion

3.1. Pyrolysis of the films

Thermal analysis of the deposited film (with formamide addition) was performed. The TGA curve shown in Fig. 2 reveals that the weight loss of the gel film from room temperature to about 140°C corresponds to the evaporation of solvent (2-methoxyethanol, boiling point 125°C). From 140°C to about 400°C , the volatilization of formamide (boiling point 210°C) and the pyrolysis of other possible organic acid residues in the film are expected. The weight loss curve then approaches flatness in the range at 400 to 650°C . Based on the above results, the sintering temperatures

for these films were determined to be in the range of 500 to 650 °C.

3.2. Properties of the films

A precursor solution containing 10 mol % Pb excess was used in order to compensate for the volatilization of Pb during the sintering process. Rapid thermal annealing using an i.r. rapid thermal annealing (RTA) furnace (Sinku-Riko HPC-7000) was used to prepare samples at short soaking times to prevent lead volatilization. Besides, Tuttle *et al.* [26] have reported that rapid heating minimized pyrochlore nucleation and inhibited its formation. This result is in agreement with the data shown in Table I in which all the films prepared by using RTA and sintered at 600 °C contained only the perovskite phase.

The sintering conditions and the structure of film deposited on Si(Pt) substrate are listed in Table I.

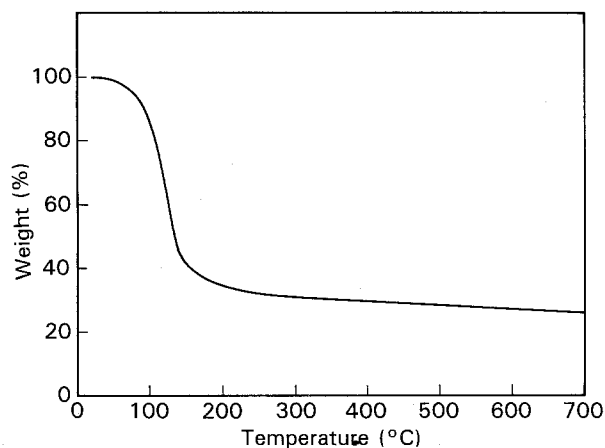
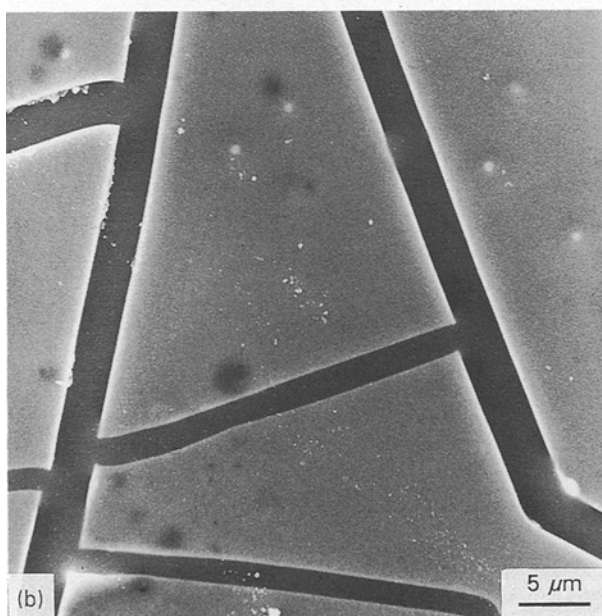
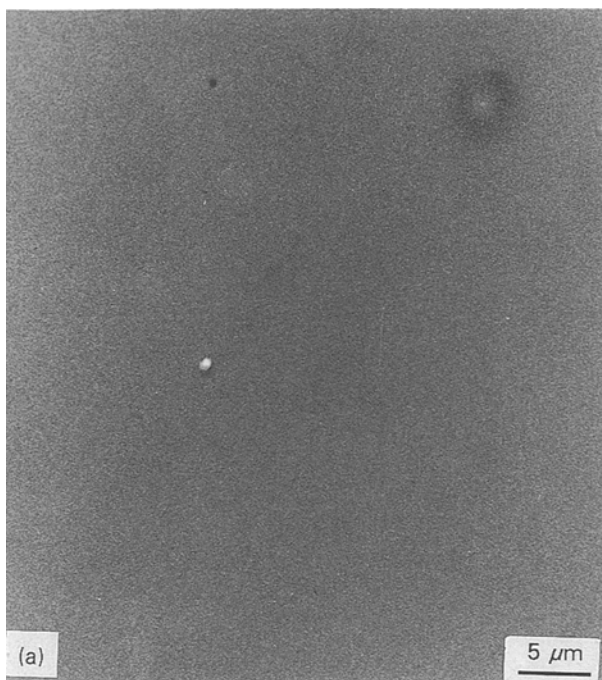
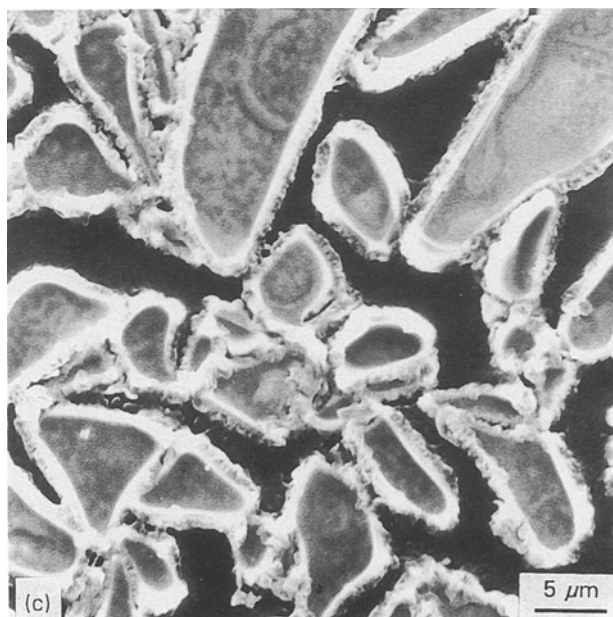


Figure 2 Thermogravimetric analysis curve of film deposited on Si(Pt) substrate.

Table I shows that whether ethylene glycol was added or not the films still cracked. Fig. 3 shows scanning electron micrographs of these films sintered at 600 °C for various sintering times. It indicates that the cracks occur after sintering and increase with increasing sintering time. The strong cross-linking effect of ethylene glycol would lead to the small pore and/or non-uniform pore size distribution in the film. The non-uniform pore size distribution of the film is expected to cause non-uniform shrinkage and cracking of the film. The surface tensions of ethylene glycol and formamide at 25 °C are 48 and 30 dyne cm⁻¹ (0.048 and 0.030 N m⁻¹), respectively. A combination of the two liquids would increase the surface tension of the solvent (2-methoxyethanol) and enhance the capillary force during drying, thus increasing the drying stress and leading to cracking. Lead evaporation also affects the film cracks. This can be verified from Fig. 3c, where the film sintered for 12 h exhibits more serious cracking.

Figure 3 Scanning electron micrographs of films prepared with ethylene glycol addition: (a) before sintering, (b) after sintering at 600 °C for 2 h, (c) after sintering at 600 °C for 12 h.



Despite the cracking problem, addition of ethylene glycol allows the perovskite phase to be formed at lower sintering temperatures. Fig. 4 illustrates the X-ray diffraction patterns of film prepared with ethyl-

ene glycol addition and sintered at 600 °C for different times. It reveals that the intensity of the perovskite phase increases with increasing sintering time. However, the thin films prepared without the addition of

TABLE I Processing conditions and resultant PLZT(8/65/35) thin films on Si(Pt) substrates

DCCA	Sintering temperature (°C)	Sintering time	Phase	Film surface
None	600	24 h	Amorphous	Cracked
	650	24 h	P, π	Cracked
	600	12 h	P, π	Cracked
Ethylene glycol	600(RTA)	2, 5, 8, 12 h	P	Cracked
	550(RTA)	12 h	Amorphous	Cracked
Formamide	600	6 h	P, π	Smooth
	600 (RTA)	1, 10, 15 min	P	Smooth
	550(RTA)	30 min	Amorphous	Smooth

P: Perovskite; π : Pyrochlore
RTA: Rapid Thermal Annealing

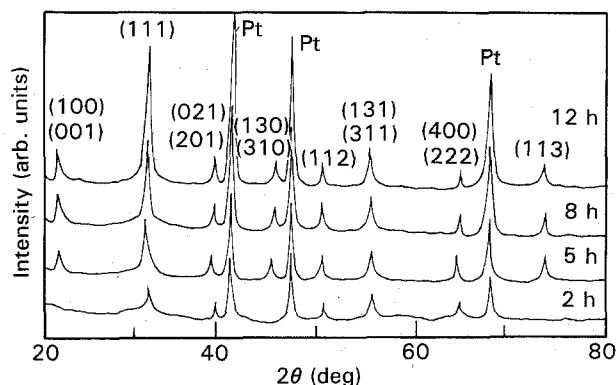
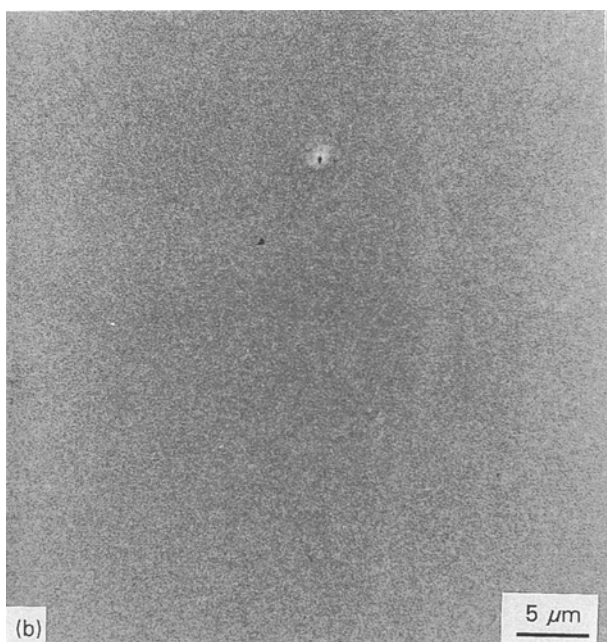
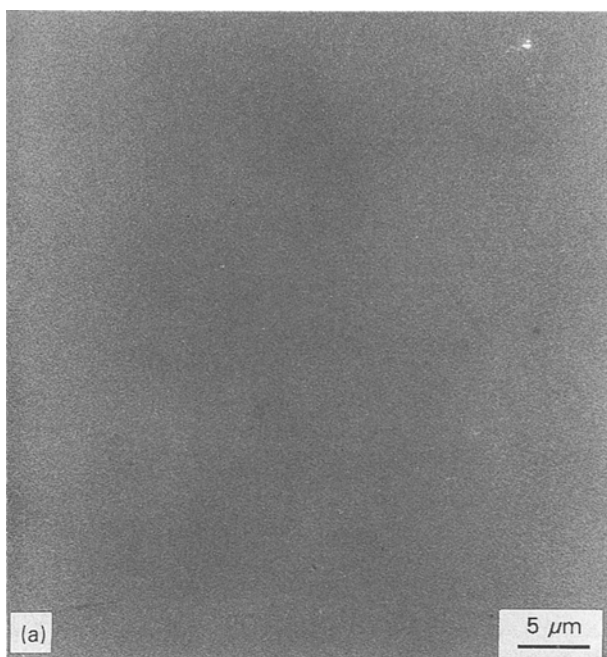
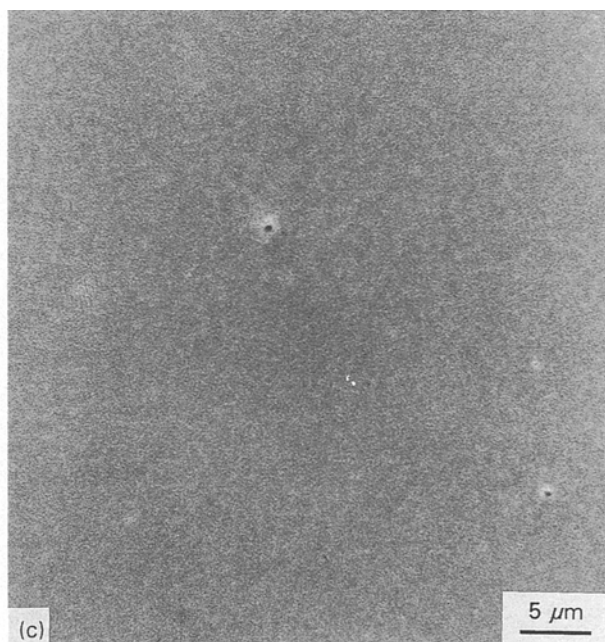


Figure 4 X-ray diffraction patterns of films prepared with ethylene glycol addition, deposited on Si(Pt) substrate and sintered at 600 °C for different times.

Figure 5 Scanning electron micrographs of films prepared with formamide addition: (a) before sintering, (b) RTA sintering at 600 °C for 1 min, (c) RTA sintering at 600 °C for 15 min.



ethylene glycol and sintered at 650 °C formed the perovskite and pyrochlore phases, but with sintering at 600 °C a crystalline phase could not be obtained. The role of ethylene glycol in the gel is expected to cause a cross-linking effect which reduces the distance between the metal atoms and leads to a reduction of the diffusion length of metal atoms. Therefore, the addition of ethylene glycol should reduce the sintering temperature needed to obtain the perovskite phase.

Because addition of ethylene glycol could not solve the crack problem of the films, formamide was used instead of ethylene glycol as a DCCA. SEM micrographs of the films prepared with formamide addition after RTA treatment are presented in Fig. 5. It indicates that continuous and crack-free films can be obtained. The addition of formamide to the precursor is

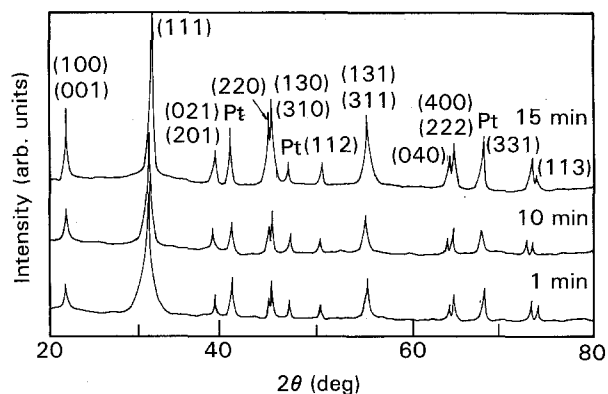


Figure 6 X-ray diffraction patterns of films prepared with formamide addition, deposited on Si(Pt) substrate and sintered at 600 °C for different times.

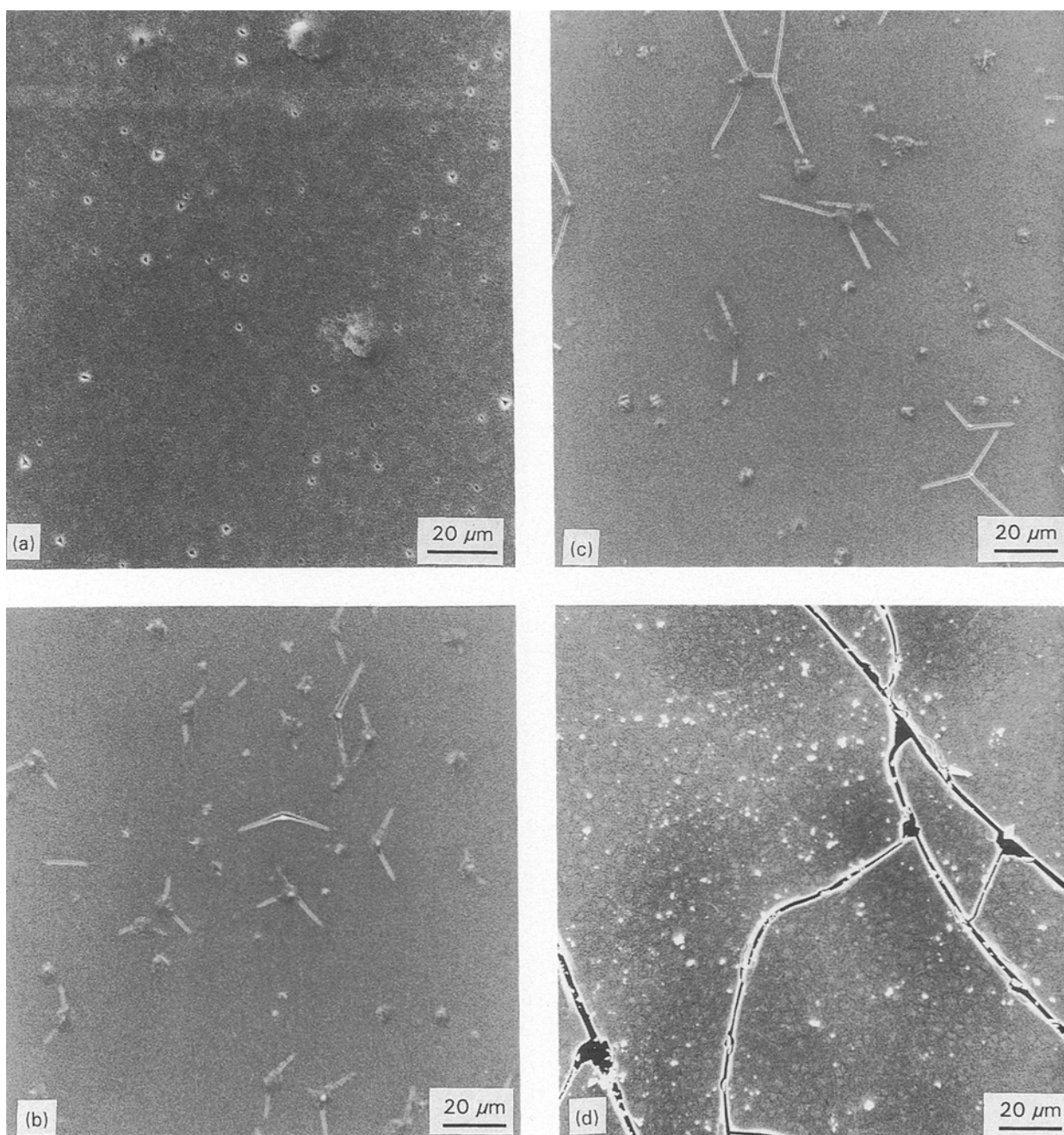


Figure 7 Scanning electron micrographs of films prepared without DCCA, sintered at 600 °C with different heating rates: (a) 5, (b) 30, (c) 40, (d) 80 °C min⁻¹.

believed not only to narrow the distribution of pore sizes but also to increase the pore size, which then reduces the drying stress and capillary pore formation [19–24]. Another possible reason is that the vapour pressure of formamide (0.1 torr at 40 °C) is lower than that of the solvent 2-methoxyethanol (20 torr at 34.3 °C). Combination of the two liquids in the precursor can reduce the rate of evaporation during the initial stages of drying, thus reducing the drying stress and preventing the film from cracking. X-ray diffraction patterns of films sintered at 600 °C by the RTA heating method are shown in Fig. 6. It indicates that the perovskite phase can be obtained after only one minute of sintering, and the amount of phase increases with increasing sintering time.

The role of formamide in the gel preparation has been extensively studied to demonstrate its effects on

the sol–gel process such as the gelation time, pore size, pore size distribution and the physical properties of the gels formed [19–24]. The different effects of ethylene glycol and formamide additions are proposed to arise as follows:

1. The molecule of formamide, $\text{H}_2\text{N}-\overset{\text{H}}{\text{C}}=\text{O}$ (molecular weight 45.04 g mol^{-1}), is smaller than that

of ethylene glycol, $\text{HO}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{OH}$ (molecular weight 62.07 g mol^{-1}), so that the molecular association after formamide has reacted with a metal-organic molecular system is smaller than that of ethylene glycol reacted with the same system. This leads to networks of the former being more closed

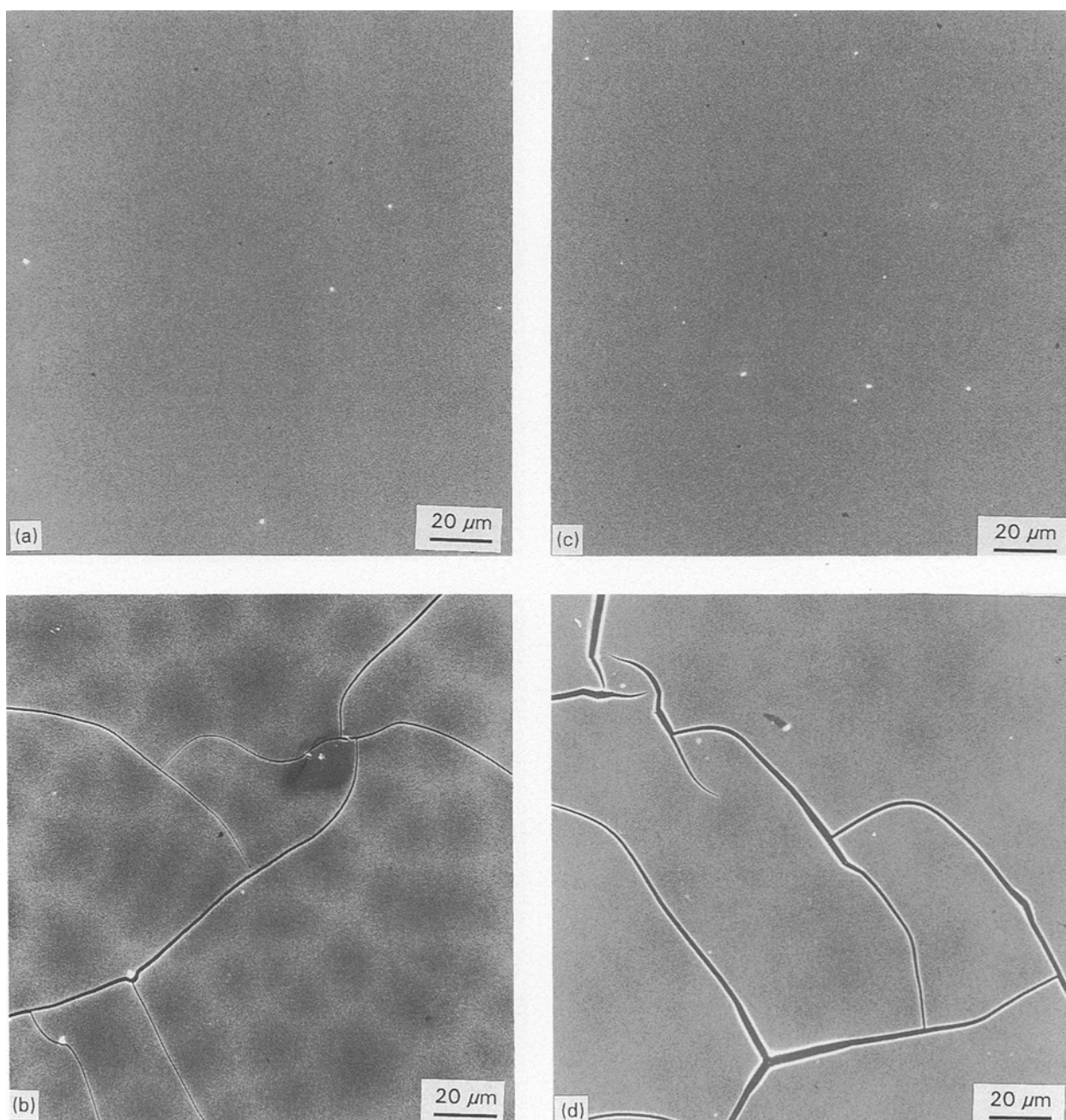


Figure 8 Scanning electron micrographs of surface morphology for films deposited on different thickness of platinum: (a) 100 nm, (b) 300 nm, (c) 100 nm, (d) 300 nm; (a, b) prepared without DCCA, (c, d) prepared with formamide.

than those of the latter. Therefore, densification of the film prepared from the formamide-containing precursor was easier and avoided crack formation.

2. By similar reasoning, the reduced sintering time resulted because the formamide possesses a hydrogen bond which reacts strongly with metal-alkoxide in the precursor solution and reduces the diffusion length. A complete interpretation of these effects require further investigation.

Crack formation took place easily in the films deposited on Si(Pt). In addition to the above-mentioned factors, many processing variables such as the rate of sintering, the thickness of platinum and the ageing time of precursor solution have important influences on the crack formation. Fig. 7 shows SEM micro-

graphs of films prepared without DCCA and sintered at different heating rates. It indicates that when the heating rate is $30\text{ }^{\circ}\text{C min}^{-1}$ or more the films formed cracks. The higher the heating rate, the more serious was the crack damage. This may be due to the rapid volatilization of solvent. As shown in Fig. 8, the films deposited on the substrate with 100 nm thick platinum are crack-free whether or not a DCCA was used. The films deposited on 30 nm platinum substrate formed cracks. The reason is that the difference in thermal expansion coefficient between the PLZT film and silicon substrate is very large. The thicker platinum layer was able to average this difference and reduce the thermal stress between them.

Gelation of the solution is related to the ageing time. Fig. 9 indicates that the longer the ageing time,

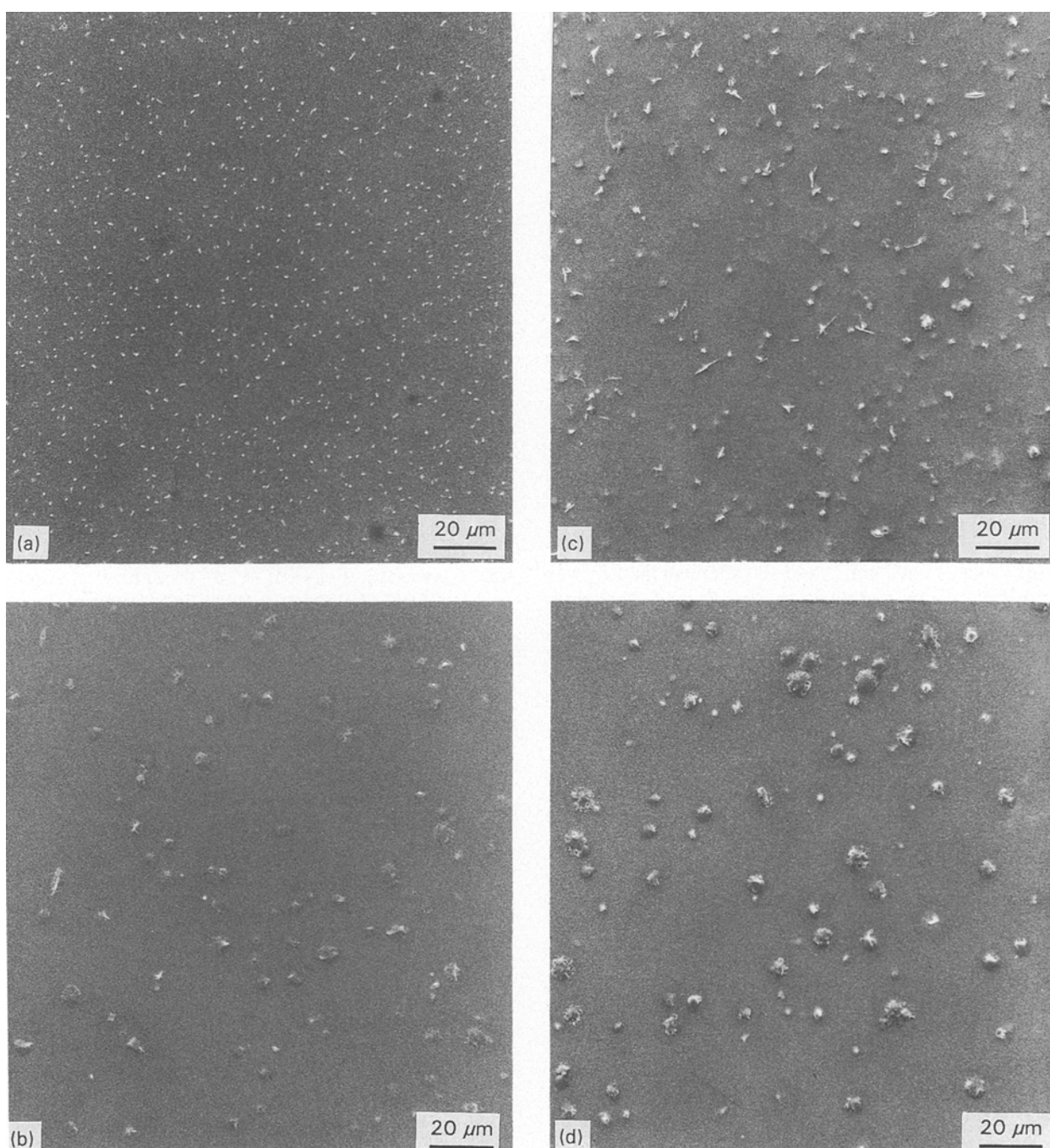


Figure 9 SEM morphology of films prepared from precursors aged for different times (a) 1 day, (b) 3 days, (c) 7 days, (d) 14 days.

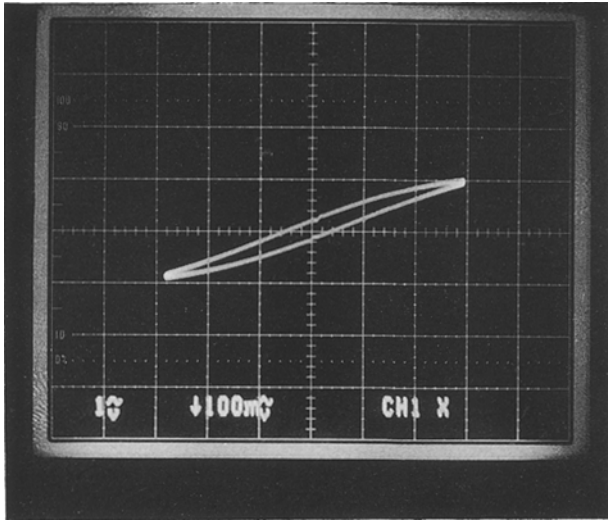


Figure 10 Hysteresis loop at 1 kHz of a PLZT(8/65/35) thin film prepared with formamide addition and sintered at 600 °C for 1 min; horizontal scale 33.4 kV cm⁻¹ per division, vertical scale 6.5 μC cm⁻² per large division.

the greater the number of precipitates formed before sintering. When the ageing time is too short (below 1 day), the gelation reactions were not complete. This led to pores in the film and crack formation after sintering. With longer ageing times, film cracking was reduced. When the ageing time was too long, it produced a precipitate. This phenomenon might be related to the prolonged hydrolysis and gelation, when the organometallic polymeric molecules may grow to form larger particles which lead to precipitation. The better gelation time with certain DCCAs should be given more detailed examination.

Fig. 10 shows a typical P - E hysteresis loop of a film prepared with formamide addition deposited on Si(Pt) and sintered by RTA at 600 °C for 1 min. The film thickness was about 300 nm. The remnant polarization P_r was 1.3 μC cm⁻² and the coercive field E_c was 15 kV cm⁻¹. In comparison the P_r and E_c values measured by Vest and Xu [16] were $P_r = 5$ μC cm⁻² and $E_c = 8$ kV cm⁻¹ (film thickness = 2.5 μm). The smaller value of P_r and larger value of E_c in this study are due to the difference in film thickness. The remnant polarization increases and the coercive field decreases with increasing thickness for PLZT films [10]. This can be explained by the presence of a space-charge layer inside each domain of grains, which is proportional to film thickness.

4. Conclusion

PLZT(8/65/35) films with a single perovskite structural phase were successfully produced by sol-gel

processing through RTA at 600 °C for only 1 min on Si(Pt) substrates. When formamide was used as a DCCA in the precursor solution it lowered the processing temperature and prevented crack formation of the films. The PLZT film showed a well-developed hysteresis loop. The remnant polarization was about 1.3 μC cm⁻² and the coercive field about 15 kV cm⁻¹.

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