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Processing and Seeding Effects on Crystallisation of PZT Thin Films from Sol-Gel Method*

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Abstract

Lead zirconate titanate PZT (52/48) thin films on alumina substrates were prepared by the sol-gel method. In order to prepare pure perovskite phase films at lower temperature, the study of the processing conditions and of seeding effects on the crystallisation behaviour of the PZT perovskite phase was carried out by X-ray diffraction and scanning electron microscopy analysis. The obtention of the perovskite phase was seen to be highly dependent on the preparation conditions of the sols. The viscosity behaviour of the stock sols was analysed by rheological studies in order to obtain data allowing verification of the stability of the stock solutions. A considerable improvement on the crystallisation of the pure perovskite phase at lower temperatures was observed when PZT seeds were added to the sols. © 1997 Elsevier Science Limited.

1 Introduction

Ferroelectric thin films of lead zirconate titanate (PZT) are of actual scientific and technological interest for use as components for non-volatile memories, electro-optic devices, pyroelectric sensors and piezoelectric transducers. For all these devices, the fundamental requirement is the growth of high quality ferroelectric films on specific substrates and electrode materials, i.e. the growth of pure perovskite phase films with optimized grain size, crystallographic orientation and thickness, adequate for each application.

The earlier PZT thin films were prepared mainly by vacuum deposition techniques such as ion beam deposition[1] and sputtering.[2] However, due to the difficulty of stoichiometry control and to the existence of a complex set of deposition parameters in such techniques, the preparation of quality films by vacuum techniques is limited.[3]

More recently, among the different possible chemical techniques to prepare thin films, the sol-gel method has been revealed as promising. It offers, as an important advantage, the possibility of an accurate control of the composition at the molecular level, together with a considerable simplicity, versatility and lower cost process.

It is well known that the perovskite phase formation of the lead-based family of materials is a sequential process, being that phase formed at higher temperature, after the appearance of a pyrochlore-type phase. For this reason, a high temperature for the post-deposition thermal treatment is required for the formation of the desirable perovskite phase. This constitutes one of the practical problems of the integration of PZT films prepared by sol-gel into the actual microcircuits technology.

Typical temperatures for the formation of the PZT perovskite phase in films vary between 650 and 750°C. At these temperatures, interdiffusion between the PZT films, the electrodes, and the underlying metallization can occur. Besides that, the thermal stresses developed at these temperatures may affect the long-term reliability of the device and, finally, some substrate materials, needed for specific applications like glass, cannot support these high temperatures.

Several attempts have been made to lower the perovskite phase formation temperature in the sol-gel derived films. These approaches include rapid heating of amorphous films up to the calcination temperature,[4–6] the deposition of a $PbTiO_3$ interlayer between the substrate and the PZT film,[7] high-pressure annealing,[8] and the choice of suitable substrate materials with appropriate lattice parameters, similar to those of the film.[9]

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Reaction kinetics studies[7,10] have shown that the phase transformation, pyrochlore – perovskite, is a nucleation controlled process, with the nucleation of the perovskite phase as the rate-controlling step of the reaction. Then, the kinetics of this reaction can be improved if the number of nucleation sites is increased. The effect of using perovskite seeds in PZT[11] and PMN[12] powders was studied and a decrease of the formation temperature of the pure perovskite phase was observed.

In accordance with this, the addition of crystalline seeds of PZT in amorphous gels of the same composition was used, in this study, to prepare monophasic perovskite PZT thin films at low temperatures.

The crystallization behaviour of the PZT phase on thin films, prepared using different precursors, stabilizers and contents of seeds, was investigated using X-ray diffraction analysis and scanning electron microscopy. The stability of the PZT precursor sols was examined by rheological studies, using a rheometer to evaluate the flow behaviour of the sols. Rheological flow curves of differently prepared sols, with and without seeds, are presented and discussed.

2 Experimental procedure

2.1 Preparation of stock precursor sols

PbAc (lead acetate trihydrate, Panreac, 99%), Zr(n-Pr) (zirconium tetra-n-propoxide, Fluka), ZrAcAc (zirconium acetylacetonate, Merck, 98%), and Ti(i-Pr) (titanium tetra-isopropoxide, Merck, ≥97%), TIAA (titanium diisopropoxide bis(2,4-pentanedionate), Aldrich, 75%) were used as starting reagents. These were dissolved in alcoholic medium with different stabilisers to form a stable precursor sol. The ratio of Zr/Ti was kept at 52/48 and the mixing procedure of the lead, zirconium and titanium precursors is shown in the flow chart (Fig. 1). Different solvents such as ethanol, acetone, ethylene glycol, propanol, 1,2-propanediol and ethanolamine (Table 2) were chosen to check their abilities to dilute the PZT precursor sol, to form a stable stock sol. It was found that to obtain a stable stock sol, a concentration of 0·4 M of the PZT precursor was suitable. The stability of the PZT stock precursor sol was analysed by a rheometer (Carri-med, CSL500). A FT-IR spectrometer (Mattson, 7000, with a 2-cm^{-1} resolution) was used to study the structure of some precursor sols.

2.2 Preparation of PZT seeds and of the diphasic sols

Fine PZT(52/48) powders were used as seeds. The PZT powder was prepared according to the procedure described in Fig. 1(b), without dilution. The sol was maintained at 60°C for several weeks until it became a transparent gel. The dried gel was calcined at 600°C for 1 h. The formation of the perovskite phase was checked by XRD analysis. The PZT powder was milled and dispersed with a suitable solvent (Table 2) and dispersant (Dispex A40; Allied Colloids, Ltd — ammonium salt of a polycarboxylic acid) for 5 h using a vibrator mill. The mean particle size of the PZT powders, about 0·3 μm, was measured by a ZetaSizer 4 (Malvern Inst. Ltd., equipped with series 7032 Multi-8 Correlator). The suspension of PZT seeds was mixed with the PZT precursor sol according to certain ratios, so that the concentration of seeds in the seeded precursor sol was 1 wt%, 2 wt%, or 5 wt% of PZT in the sol, companied with vigorous stirring and followed by a 20 min ultrasonic treatment. The stability of the PZT suspension sols was measured with a rheometer.

2.3 Preparation of sol-gel derived films

PZT (52/48) films were prepared by dip-coating upon alumina substrates using a withdrawal speed of $\sim 4\,\mathrm{mm\,s^{-1}}$. The films were dried at 120°C for 30 min and fired between 350 ~ 700°C for 1 h in air to decompose residual organic matter, to crystallise the perovskite phase and to densify the film. SEM (Hitachi, S-4100) and XRD (Rigaku, Geigerflex D/Max-B) analyses were used to characterise the obtained films. The relative amounts of pyrochlore (Py) and perovskite (Pe) phases were determined by measuring their respective 100% intensity peaks. The perovskite content of the fired films was semi-quantitatively determined by

$$\text{`\% perovskite'} = \frac{I_{(110)}(\mathrm{Pe}) \times 100}{I_{(110)}(\mathrm{Pe}) + I_{(222)}(\mathrm{Py})}$$

3 Results and discussion

3.1 Processing effect on crystallisation of PZT thin films

In the lead-based perovskite systems, a pyrochlore-type phase is generally formed prior to the perovskite phase during the firing of sol-gel derived PZT thin films. The non-ferroelectric behaviour of this pyrochlore phase damages the electrical characteristics of the film if it persists in the final product.

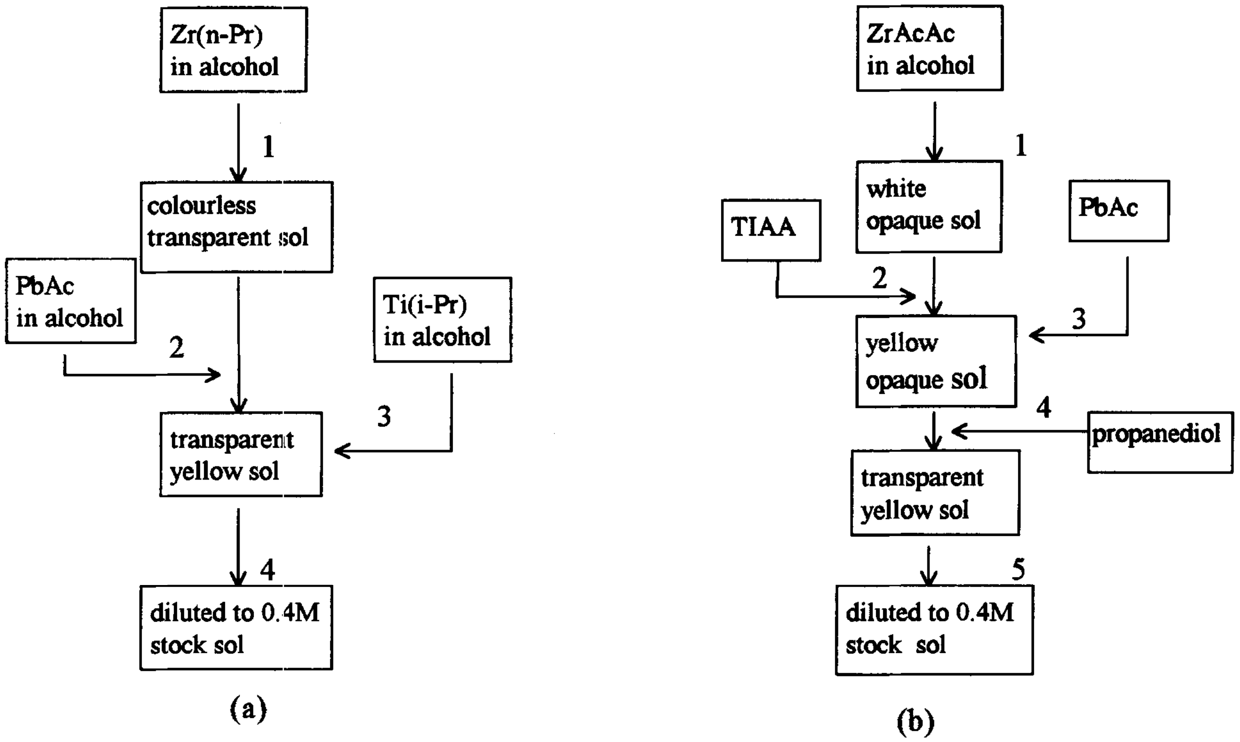

Fig. 1. Sol-gel processing for the preparation of PZT precursors: (a) using Ti(i-Pr) and Zr(n-Pr) as start chemicals (b) using TIAA and Zr(AcAc) as start chemicals.

Preliminary results showed that the crystallisation of pure perovskite phase was very dependent on the preparation conditions of the sol, such as starting chemicals, details of the processing procedure, nature and amount of the stabilisers and on the heat treatment temperatures.

Table 1 shows the comparison of the crystallisation results of some precursor sols obtained with different preparation conditions. Figure 2 shows the XRD patterns of the films derived from those precursor sols.

The pure perovskite phase is obtained at 600°C for precursor Y1 and Y3, and at 700°C for precursor Y2 and Y4.

Among these precursors, sol Y1, prepared from Zr(n-Pr)[a] (undiluted), shows high stability. It remained transparent for more than six months, indicating the absence of any gelation phenomena. Although it became opaque after 11 months, it was still possible to prepare coatings with it, where the desired pure perovskite phase could be detected after calcination at 600°C. The viscosity of the precursor sol Y1 varied only slightly during the ageing process (Fig. 3), its value approximately 0·011 Pa·s. The infrared spectrum of sol Y1 showed no obvious structural changes after that ageing period, as shown in Fig. 4.

Several characteristic absorption bands can still be assigned from the rather complex IR spectra shown in Fig. 4. An absorption band at 1554 cm^{-1} can be assigned to the formation of Zr-and Ti-Acetylacetonate chelates.[13–15] These type of compounds are quite stable and may be responsible for

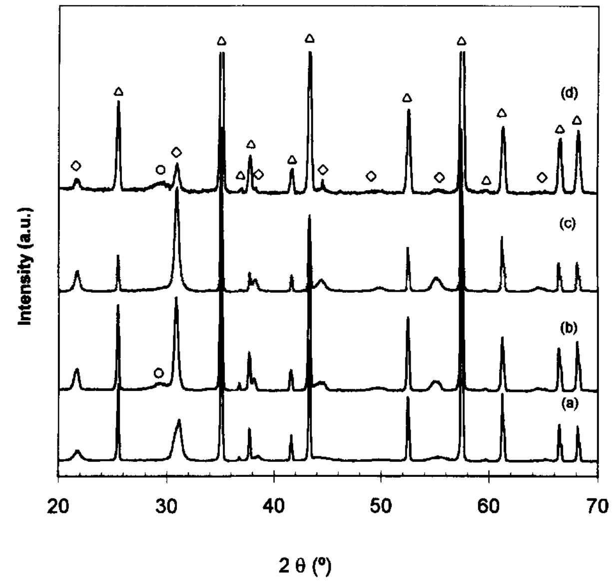

Fig. 2. XRD patterns of PZT films derived from different precursor sols after firing at 600°C for 1 h: (a) Y1 (b) Y2 (c) Y3 (d) Y4. (△-alumina substrate ◇-perovskite phase ○-pyrochlore phase).

Table 1. Crystallisation results of the films derived from differently prepared precursors

PZT precursor sol designation	*Raw chemicals*	*Diluted with*	*Stability of sols*	*Phase formed for a single layer film, fired at 550°C/1 h*	*Phase formed for a single layer film, fired at 600°C/1 h*	*Phase formed for a single layer film, fired at 700°C/1 h*
Y1	PbAc Ti(i-Pr) Zr(n-Pr)[a]	Acetone	≤11 month transparent sol; after 11 months opaque sol	Pe + Py '% Pe' = 90·0	Pe '% Pe' = 100	Pe '% Pe' = 100
Y2	PbAc Ti(i-Pr) Zr(n-Pr)[b]	Acetone	> 8 month transparent sol	Pe + Py '% Pe' = 96·18	Pe + Py '% Pe' = 96·53	Pe '% Pe' = 100
Y3	PbAc TIAA ZrAcAc	Ethanol	> 2 month transparent sol	Pe + Py '% Pe' = 93·38	Pe '% Pe' = 100	Pe '% Pe' = 100
Y4	PbAc TIAA ZrAcAc	Acetone	1·5 month transparent sol; after 1·5 months opaque sol	Pe + Py '% Pe' = 90·5	Pe + Py '% Pe' = 97·4	Pe '% Pe' = 100

[a] Zr(n-Pr)–Zirconium propoxide (undiluted),
[b] Zr(n-Pr)–Zirconium propoxide (diluted in propanol, ~70%), Pe–perovskite, Py–pyrochlore

the absence of structural change in the sol Y1 during the 11 months ageing. Also, an absorption band present at 1710 cm^{-1} can be assigned to the C = O stretch of acetic acid.[16] Earlier studies[17,18] have shown that in the preparation of PZT precursor, the replacement of acetic group by alkoxy groups resulted in the formation of either free acid or ester in the reactions:

$$\mathrm{PbAc + ROH \rightarrow PbOR + HAc}$$

$$\mathrm{HAc + ROH \rightarrow AcR + H_2O}$$

Where R represents -$CH_2OCH_2CH_3$ group, and Ac represents CH_3COO^- group. The formation of the ester (AcR) decreases the stability of the obtained sol because it is accompanied by the formation of a certain amount of water, which will cause a hydrolysis reaction. Since neither the carbonyl stretch band of the unconjugated ester (C = O) nor the acetate carbonyl-oxygen stretch

and at 1740 cm^{-1} and 1250 cm^{-1},

respectively,[16,18] were observed, it seems that, in the present experimental conditions, the ester formation was less favoured, which might also explain the high stability of the sol.

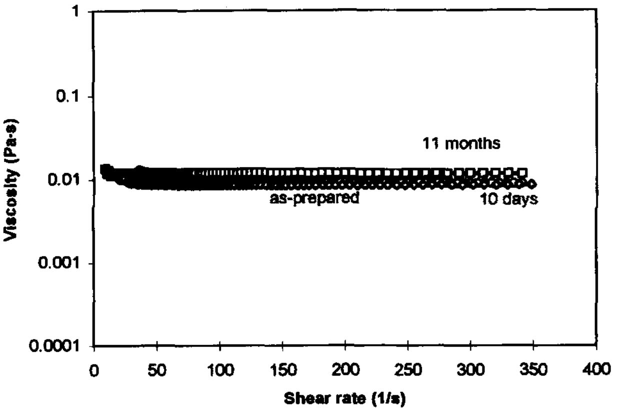

Fig. 3. Plots of viscosity versus shear rate for PZT precursor Y1 with different ageing time (as-prepared, 10 days, and 11 months).

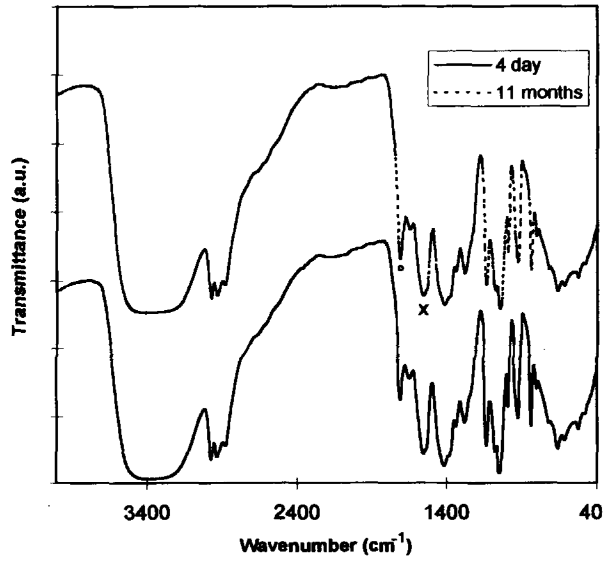

Fig. 4. FT-IR spectra of precursor Y1 with different ageing time (x-absorption band at 1554 cm^{-1}, o-absorption band at 1710 cm^{-1}).

When zirconium propoxide diluted with propanol (Zr(n-Pr)^{II}) was used for the preparation of the PZT precursor Y2, some fine transparent gel particles were formed during the mixing step, and for that reason it was difficult to peptise. In this case, long heating times had to be employed to obtain a transparent sol. While in films derived from Y1 the pure perovskite phase crystallises at 600°C, in films derived from Y2 there is still some pyrochlore phase at that temperature (Fig. 2). This might be attributed to the existence of microheterogeneities produced during the mixing process (step 2) leading to preferential self-condensation of the zirconium precursor instead of co-condensation[19] of the Pb–Zr–Ti precursor. Therefore, a segregation of a PT-based pyrochlore phase can occur in this condition. Further structural investigation is being carried out on this matter.

Precursor Y3 and Y4 were prepared using TIAA and ZrAcAc diluted with different solvents (Table 1). The films derived from precursor Y3 showed lower crystallisation temperature for the pure perovskite phase (600°C) than that derived from precursor Y4 (700°C), and precursor Y3 is stable for a longer time than precursor Y4. In the case of these precursors, ethanol showed a better stabilization effect than acetone. The effect of the chemistry of the sol preparation on the crystallization behaviour was studied for undiluted sols and the results will be published elsewhere.

3.2 Solvent effect on the stability of the PZT stock sol and on the dispersibility of PZT powders

In the development of an industrial processing system of sol-gel preparation of materials, the cost, the availability and the toxicity of the precursors must also be carefully considered and the obtention of stable stock sols is of major importance.

The selection of the studied solvents was based on the following requirements:

(1) the solvent should maintain the PZT precursor solution stable (no condensation and agglomeration should occur and the viscosity of sol should be maintained constant);
(2) the solvent and the dispersant should have mutual solubility in order that the PZT powders can be well dispersed in the sol.

The solvents that satisfied condition (1) can be used to dilute the PZT sol and to make a stock sol (without seeds). The solvents that satisfied condition (2) can be used to make a PZT suspension (with seeds).

Table 2 shows the experimental results of some selected solvents used to prepare the stock sols. The changes of the solution behaviour were followed by rheological studies and the flow curves are shown in Figs 5 and 6.

The rheological behaviour of the PZT sol mixed with ethyleneglycol, with different ageing time, is presented in Fig. 5. It was observed (Fig. 5(a)) that, for a short ageing time (sample as-prepared and sample aged for 6 h), the viscosity was almost independent of the shear rate and the sols exhibit nearly Newtonian flow behaviour (Fig. 5(b)). After longer ageing time (30 h), a shear thinning behaviour was observed, with the apparent viscosity decreasing as the shear rate increases.

The initial stage of hydrolysis/condensation growth of polymeric species is similar to the addition of particles to a pure liquid. The presence of 'particles' (i.e. polytitanate species) in a flowing liquid produces perturbation in the liquid streamlines. For a given shear rate, the rate of energy dissipation is increased and a high shear stress (and therefore a high viscosity) is measured relative to that of the pure liquid. For a low polymeric

Table 2. Effect of the selected solvents on the stability of sols

Solvents	*Mixed with PZT precursor sol (Y2)*	*Observation/comments*	*Mixed with dispex A40*
Ethanol	stable for more than 3 months	solution/can be used to dilute precursor sol to make stock sol	not soluble
Acetone	stable for more than 3 months	solution/can be used to dilute precursor sol to make stock sol	not soluble
Ethylene glycol	not stable, easy gelation	transparent gel, (3 days later, sol became unmovable)/not suitable	soluble
Propanol	stable for a short period of time	transparent gel (8 days later sol gelified)/not suitable	not soluble
1,2-propanediol	stable for more than 1 month	solution/can be used to dilute sol and to disperse powder to make suspension	soluble
Ethanolamine	stable for a short period of time	solution + precipitate, (5 days later, precipitate occurs in sol)/not suitable	soluble

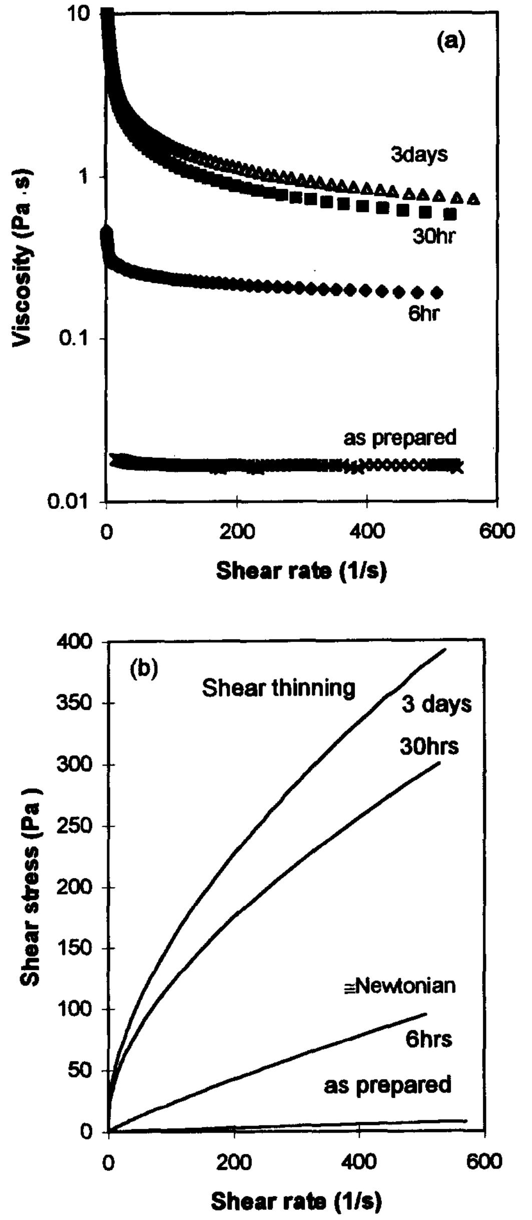

Fig. 5. Plots of viscosity versus shear rate (a) and shear stress versus shear rate (b) for the PZT precursor mixed with ethylene glycol with different ageing time (6 h, 30 h, and 3 days).

concentration, the flow behaviour is not much influenced by the 'particle-particle' (or polymer–polymer) interactions and a Newtonian behaviour is still observed (as-prepared sol and sol aged for 6 h). With further ageing (30 h and 3 days), agglomeration of polyspecies occurs, leading to an increase in the viscosity (Fig. 5(a)) due to immobilised liquid within the interparticulate void space. As the shear rate is increased, the breakdown of agglomerates occurs, releasing the immobilised liquid and resulting in lower viscosity (Fig. 5(a)). This is reflected in the observation of a shear thinning flow behaviour (Fig. 5(b)) that points to the existence of agglomeration of polyspecies in the sol.

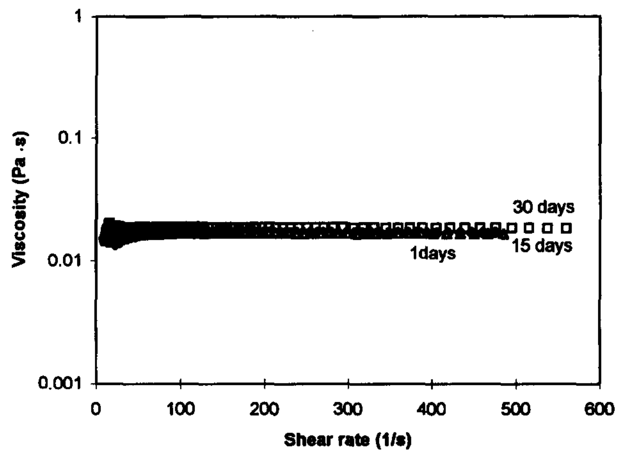

Fig. 6. Plots of viscosity versus shear rate for a PZT suspension with 2 wt% of seeds with different ageing time (1, 15, and 30 days).

Though some researchers[20,21] reported that ethylene glycol can be used as a solvent to dilute and stabilise PZT precursors, in the present study it was seen that the addition of ethylene glycol to the PZT sol increases the sol viscosity until it finally gelified. From these results, it can be concluded that the addition of ethylene glycol to the PZT sol is not always efficient to restrain hydrolysis/condensation/agglomeration stage.

The addition of ethanolamine and propanol to the PZT sol results in a similar situation, but the stability of the solution is maintained for a longer period of time than for ethylene glycol (Table 2).

It was found that a PZT precursor (Y2) is quite stable if diluted with acetone, ethanol and 1,2-propanediol (Table 2). The rheological behaviour of a PZT sol (Y1) mixed with acetone and aged for different periods of time, presented in Fig. 3, highlights the high stability of the stock sol, even after being stocked for 11 months.

It was also found that 1,2-propanediol is quite suitable to make a suspension of PZT powders. Figure 6 shows the plot of the viscosity versus shear rate of the PZT suspension -PZT precursor solution with 2 wt% seeds, for different periods of ageing. After mixing, the viscosity of the suspension is stable at least for one month, which means that the evolution stage of hydrolysis/condensation/agglomeration is sluggish or retarded. Similar viscosity behaviour was observed for the other seeded suspensions.

3.3 Seeding effect on crystallisation of PZT thin films

The addition of seeds to the precursor sol was performed as described in 2.2 and the ratio of addition

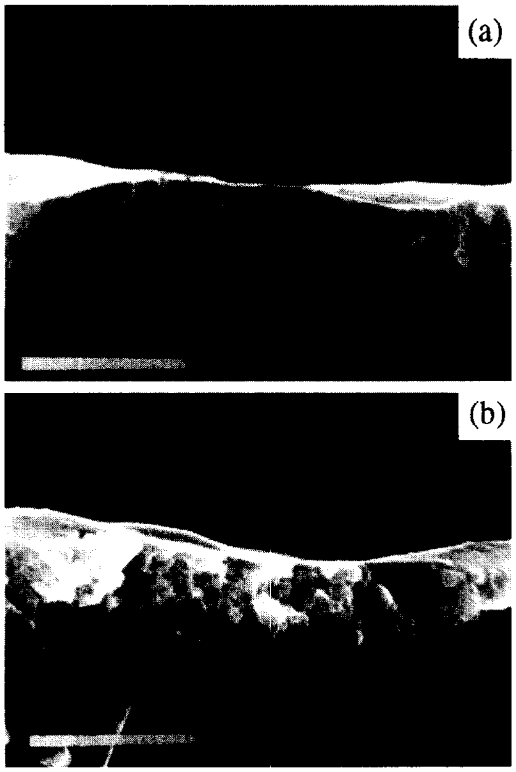

Fig. 7. SEM micrograph of PZT films on cross-section obtained from (a) precursor Y2 without seeds, heat treated at 700°C/1 h (b) precursor Y2 with 1 wt% seeds, heat treated at 550°C/1 h. (bar = 1·5 μm).

was 1, 2 and 5 wt%, respectively. The films derived from these precursors have similar thickness, around 0·5 μm, as verified by SEM observation (Fig. 7).

Figure 8 gives the evolution of the relative content of the perovskite phase, calculated from the 100% XRD intensity peaks, with the heat treatment temperature.

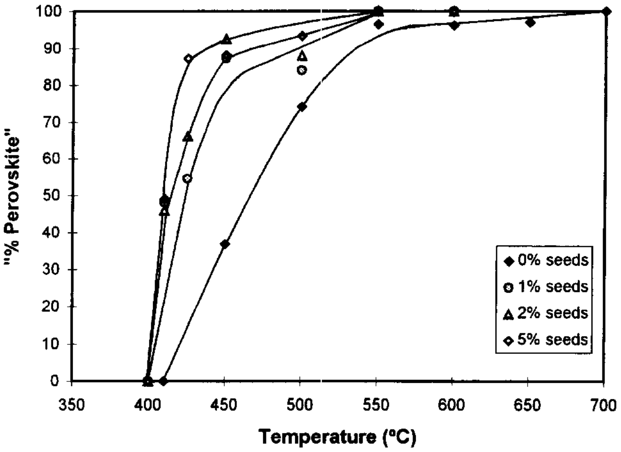

Fig. 8. Percentage of perovskite phase versus temperature for PZT films derived from precursor Y2, with various concentration of seeds.

The effect of seeds on the crystallisation of the perovskite phase is obvious. Without seeds, the pyrochlore phase forms at 410°C, followed by the perovskite phase formation around 450°C. The presence of this pyrochlore phase persists until 650°C. The pure perovskite phase will be obtained only after firing at 700°C (Fig. 8). With the addition of 1~5 wt% of seeds, the perovskite phase formation starts earlier, at around 410°C, and the temperature at which the pure perovskite phase is present decreases to 550°C (Fig. 8).

From the growth kinetic theory for crystallisation and for samples with the same composition, the influence of the number of nuclei (N) on the crystallisation temperature (T_p) can be expressed by[22]

$$\ln N = E/R\ (1/T_p) + \text{constant} \qquad (1)$$

E being the activation energy for crystal growth, and R is the gas constant.

That is, as the number of nuclei increases, the lower is the crystallisation temperature. Therefore, the seeding effect can be explained by the fact that there are countless nucleation sites distributed in the films and, as a result, the regions around the seeds crystallised very quickly. Since the seeds have the perovskite structure, the perovskite phase formation in the film is promoted by epitaxial effects. The ease of nucleation is reflected in the perovskite formation temperature.

Figure 9 represents the microstructure of the unseeded films heat treated at 450°C h^{-1}. The lower magnification microphoto (Fig. 9(a)) shows, besides the alumina substrate, well identified by its grain-like structure, an amorphous, sometimes fractured film and some egg-shaped volumes, magnified on Figs 9(b) and (c). EDS analysis of the small particles on these egg-shaped volumes revealed a lead- and titanium-rich phase. XRD analysis of these 450°C heat treated unseeded films shows, besides a poor degree of crystallization, a phase content of ~63% of pyrochlore and ~37% of perovskite. The microstructure of the seeded films heat treated at 450°C is more homogeneous (Fig. 9(d)) with no egg-shaped volumes, although fractured. These observations are in agreement with the XRD analysis results showing ~90% of perovskite phase for these unseeded films.

Since the perovskite formation temperature begins at 410°C for seeded films, different firing times at that temperature were used to check their effect on the amount of the perovskite phase in the films. This effect is shown in Fig. 10.

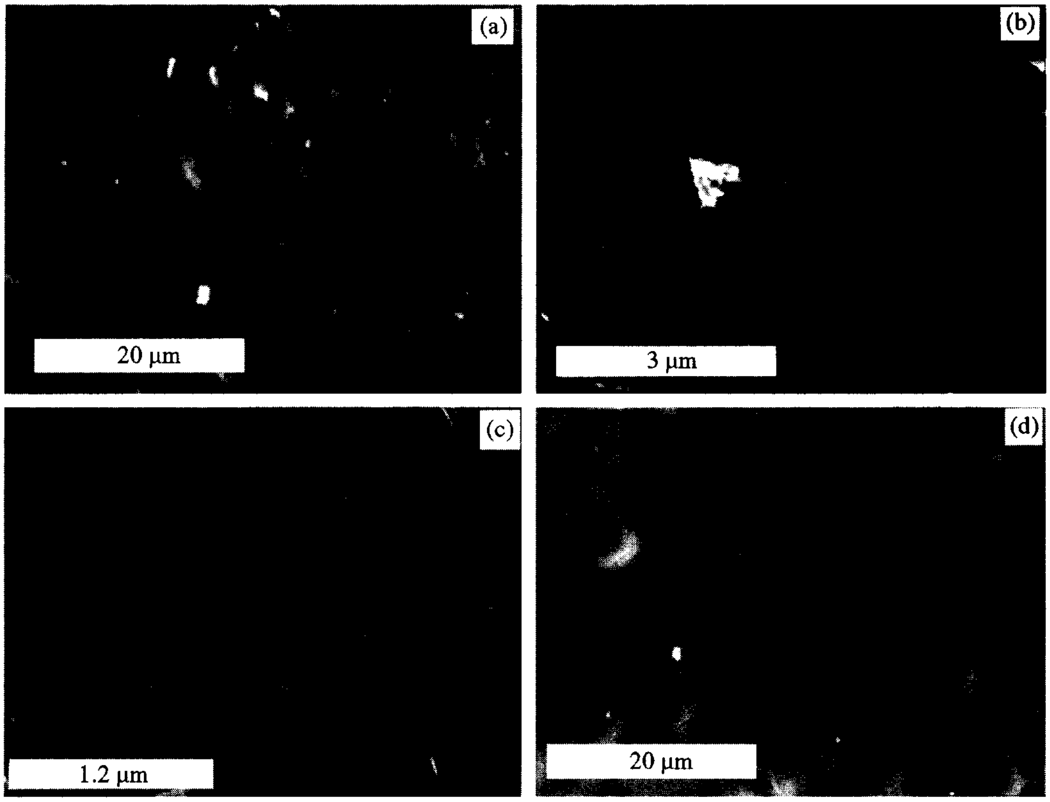

Fig. 9. SEM micrographs of top surface PZT films obtained from precursor Y2 without seeds (a, b, c) and with 5 wt% seeds (d), heat treated at 450°C/1 h.

For the unseeded film fired at 410°C, the perovskite phase was detected only after ~3 h of firing and its amount slowly increases after that, reaching only 82% after 30 h of heat treatment. Differently, for the seeded films, almost 100% of perovskite phase was obtained after 30 h of firing time. For these seeded samples, the content of the perovskite phase rapidly increases until 5 h (85~90%), followed also by a slow increase. These results are quantitatively in agreement with the modified Johnson-Mehl-Avrami equation:[23]

$$-\ln(1-x) = (kt)^n \qquad (2)$$

where x is the fraction of crystallised phase at time t, n is the reaction order which relates with the mechanism of the process, k is related to the temperature T by an Arrhenius-type equation:

$$k = AN\ \exp\ (-E/RT) \qquad (3)$$

where A is a constant. For the same temperature, the fewer nuclei (N), the smaller value of k, and therefore a longer time is needed to form the same fraction of the crystallised phase.

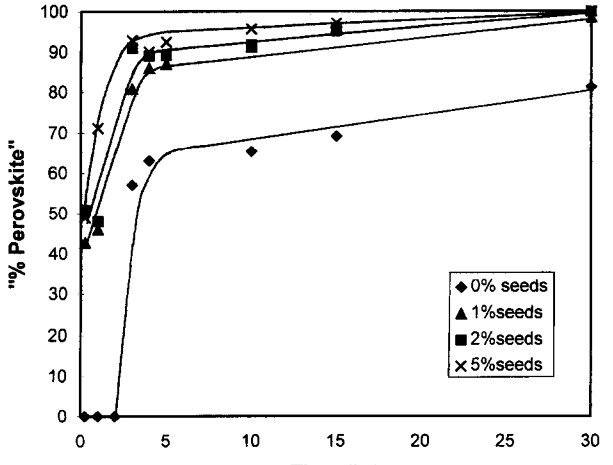

Fig. 10. Percentage of the perovskite phase versus firing time at 410°C, for PZT films derived from precursor Y2 with various concentration of seeds.

Seeding effects were also studied on the other precursor sols, Y1 and Y3, and similar effects were observed after addition of seeds. The variation of the relative amount of the perovskite phase with the heat treatment temperature is presented in Figs 11 and 12, respectively. Relatively to the unseeded sol, the addition of 2 wt% of seeds lowers the formation temperature of the perovskite phase and also the temperature at which the pure perovskite phase is obtained, in both sols.

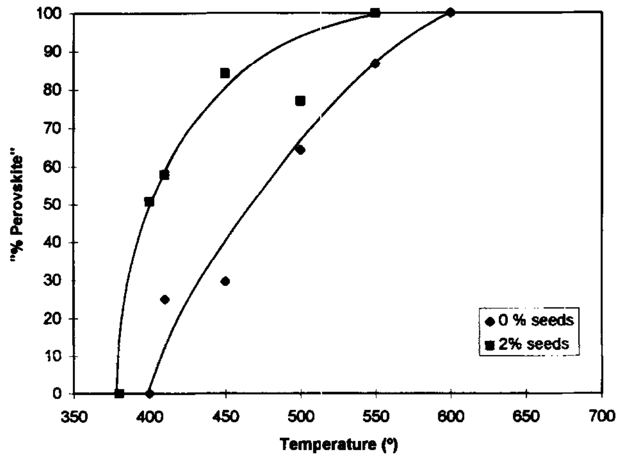

Fig. 11. Percentage of the perovskite phase versus temperature for PZT films derived from precursor Y1, with various concentration of seeds.

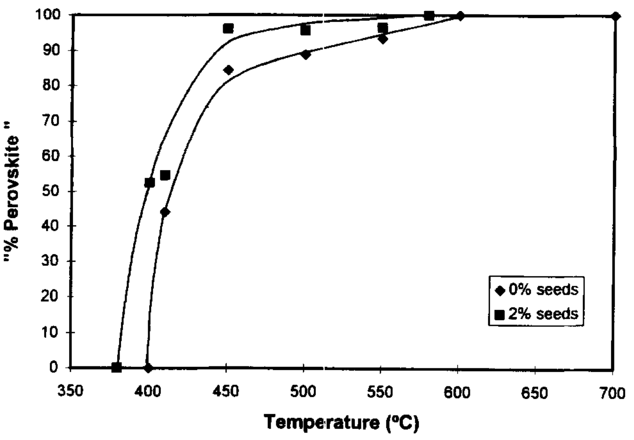

Fig. 12. Percentage of the perovskite phase versus temperature for PZT films derived from precursor Y3, with various concentration of seeds.

Since the films derived from these precursors have already higher pure perovskite content at lower temperature than those obtained from Y2, the seeding effects in Y1 and Y3 were not as considerable as in Y2.

It has been shown[10,24] that the perovskite phase is heterogeneously nucleated preferentially at the substrate-film interface, the nucleation being more difficult at the substrates where the lattice mismatch is large. From the results here presented, it seems that the seeded PZT precursor method can be used to make pure perovskite PZT films at relatively low temperatures on substrates where a large lattice mismatch would not allow its crystallisation at suitable temperatures.

4 Conclusion

Thin films with the composition PZT(52/48) have been obtained on alumina substrates by sol-gel, using different starting chemicals. The obtention of the pure perovskite phase was highly sensitive to the preparation conditions of the sols. With the selection of a suitable solvent, a PZT precursor stock sol stable for more than 11 months was obtained. The addition of PZT seeds to the precursor sols was seen to be very effective for the crystallisation enhancement of the pure perovskite phase at lower temperatures.

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