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Dip-coating conditions and modifications of lead titanate and lead zirconate titanate films

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The modifications of dip-coated lead titanate (PT) and lead zirconate titanate (PZT) films strongly depend on the film thickness and the substrate in addition to the heat-treatment temperature. At 500 to 600° C, metastable paraelectric pyrochlore grew on glass plates (amorphous plates) when the thickness of the coated films produced by one coating cycle was below 100 nm, while ferroelectric perovskite formed on crystalline substrates or when thick films were coated on amorphous plates. This tendency is discussed in terms of an inhomogeneous reaction and the epitaxial effect. The perovskite PT films coated on single-crystal $SrTiO_3$ plate at 700° C were strongly oriented to the *c*-axis.

1. Introduction

Ferroelectric lead titanate (PT), lead zirconate titanate (PZT) and lanthanum-doped PZT (PLZT) films have a broad application in various optical, thermal and mechanical sensors and in electrical and optical devices. PT and PZT have two crystal forms, stable ferroelectric perovskite (tetragonal) and metastable paraelectric pyrochlore (cubic). Because modifications of the films directly affect their properties, it is very important to ascertain whether or not the modification can be effectively controlled in the deposition process. So far, r.f. and ion sputtering (PVD) [1–5], chemical vapour deposition (CVD) [6–9] including an organometallic process [8] and a sol-gel method [10, 11] have been reported for the preparation of PT and PZT films. In the PVD and CVD processes, the modification of the films can be easily controlled by the deposition temperature, and the perovskite films tend to grow above ~ 500° C. However, it seems to be difficult to keep the shoichiometry of the deposits constant over long time periods in the PVD and CVD, and to find suitable volatile lead species, especially in the CVD process. On the other hand, the dip-coating process is very effective in the preparation of multicomponent oxide films because of the ease with which the composition of the deposits can be controlled. However, in both the sol-gel process and dip-coating method no reports on the relationship between the deposition condition and the modification of the films had been published until our previous paper [12], in which the growth conditions of the perovskite and pyrochlore films were briefly described. Here we describe in detail the relationship between the coating conditions and the modifications of the films formed, selecting the coating of PT films as the representative case.

2. Experimental procedure

The experimental procedure and the reagents used during this study were almost the same as those in the previous report [12]. 0.1 to 0.5 M PT or PZT sols which were derived from titanium isopropoxide (and zirconium *n*-butoxide), lead acetate trihydrate, and diethanolamine in isopropanol were used for the coating. In order to ensure perfect homogeneity of the sols, they were sometimes heated to the boiling point of isopropanol, but no particular effects of the heating were seen on the modifications of the films formed. In addition to glass and platinum plates, several single-crystal plates were also examined as substrate plates in order to clarify their effects on the modifications and orientation of the film formed. These were alumina (1 0 0), (0 0 1) and (1 0 1), magnesia (1 0 0), rutile (1 0 0) and (1 1 0), YSZ (1 0 0), and $SrTiO_3$ (1 0 0). These plates were washed in acetone before use.

Our system can be extended to the preparation of lanthanum-doped (PLZT) films ($Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$) by dissolving lanthanum nitrate, $La(MO_3)_3 \cdot 1.5H_2O$, in the solution, so this film was partly examined in a similar manner to PT films.

3. Results and discussion

It has been found in the PVD and CVD of PT films that the deposition temperature was one of the most effective factors in determining the modifications of the films, therefore the temperature effect was examined first. The effect of heat-treatment on the modifications of the PT films which were coated on glass plates using 0.2 M PT solution is shown in Fig. 1. Crystalline PT films could be obtained above 450 to 500° C. It is easily seen that near 500° C pyrochlore grew along with the perovskite. At this temperature, the (0 0 1) diffraction peak of the perovskite is missing, and the (1 0 1) and (1 1 0) diffraction peaks had nearly equal intensities, suggesting partial orientation to the *a*-axis. Around 550° C the pyrochlore disappeared, and only the perovskite formed, as in the CVD and PVD processes; at the same time the (0 0 1) diffraction

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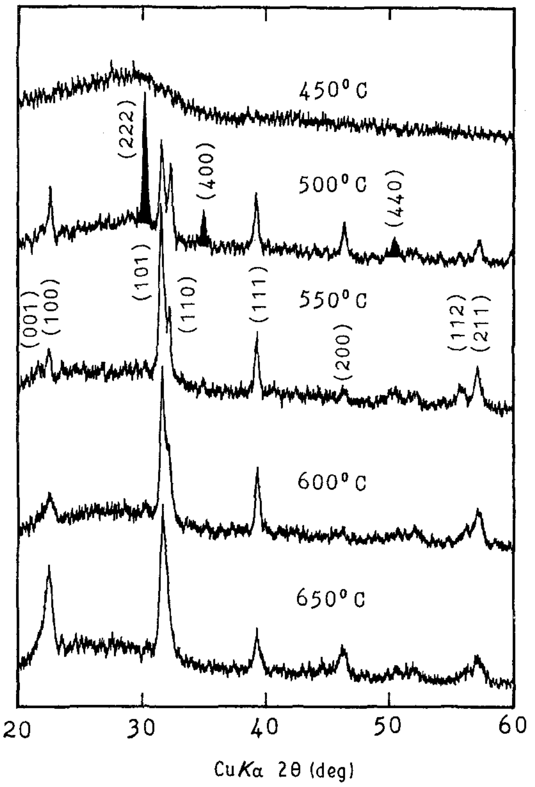

Figure 1 Effect of heat-treatment temperature on the modification of PT films formed using a 0.2 M solution. The XRD peaks shaded black were assigned to the pyrochlore. $R = 1$, $W = 3$.

peak appeared and the (1 0 1) peak intensity increased. At higher temperatures the diffraction peaks were broadened, probably due to a stoichiometry deviation through the diffusion of lead species from the film into the glass substrate as described previously [12]. However, this stoichiometry deviation has no effect on the modifications of the PT powders formed, as shown in Fig. 2, in which the XRD patterns of the PT powders derived from the gels with Pb/Ti ratios other than unity are reproduced. In every case only the perovskite-type XRD pattern was found, except for the case of excess PbO.

The CVD and PVD are thought to be fundamentally kinetically controlled processes, while the sol–gel process must be thermodynamically controlled. However, as shown here, the critical temperatures, above and below which modification of the films was varied, interestingly seem to be almost the same in both the former and latter processes. However, as shown in Fig. 3, around the critical temperature of 500° C in the dip-coating method, modifications of the films on the glass plates depend on the concentration of the components in the dip-solution used for the coating: the lower the concentration of the solution, the more easily pyrochlore forms. At 0.1 M, pure pyrochlore films were found to be deposited.

The metastable pyrochlore films should be transformed by the heat-treatment at higher temperatures. They could be readily converted to perovskite to a great extent when heated at 600° C for 24 h, and completely at 700° C for 24 h. It is interesting in this case that the annealed perovskite films had very weak (1 0 1) and (1 1 0) XRD diffraction peaks, as shown in Fig. 4, indicative of some orientation of the film.

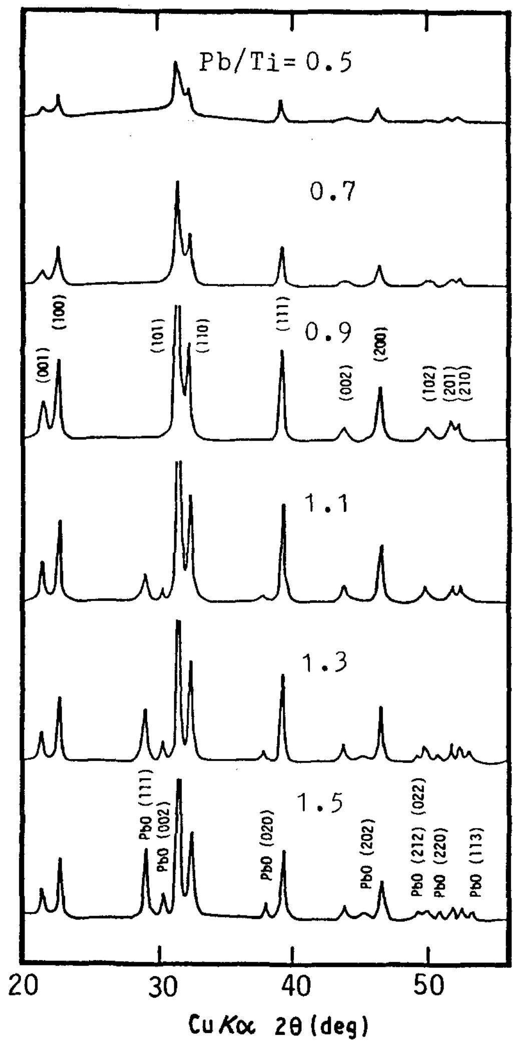

Figure 2 XRD patterns of PT powders derived from gels with different Pb/Ti ratios.

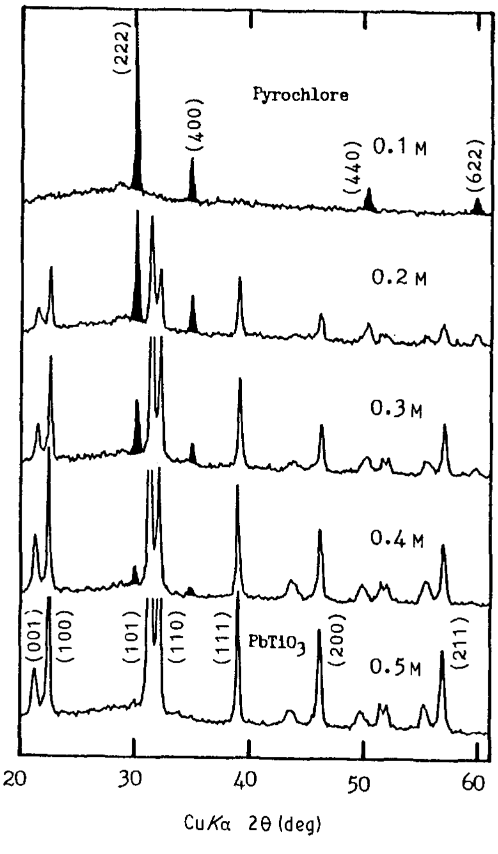

Figure 3 Effect of the concentration of the dip solution on the modifications of PT films formed at 500° C. $R = 1$, $W = 3$.

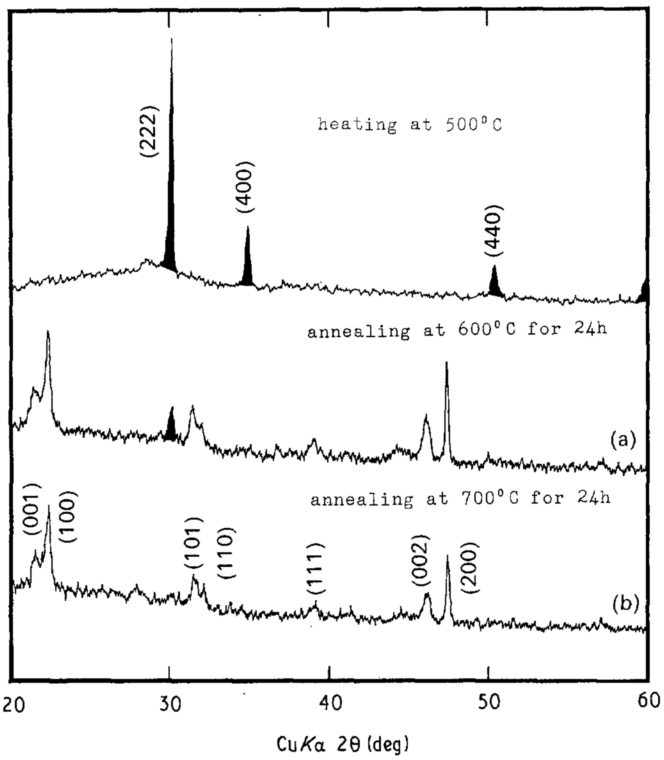

Figure 4 Transformation of a pyrochlore film to perovskite by annealing at (a) 600° C for 24 h, and (b) 700° C for 24 h.

The concentration of the dip-solution governs directly the thickness of the coated films. Fig. 5 shows the relationship between the film thickness per single coating and the concentration of the dip solution in the PT film coating. When Fig. 5 is compared with Fig. 3, it is easily seen that pyrochlore formation becomes remarkable when the thickness of the film on the glass plate was below 100 nm per single dip-coating. Lead species in the films on the glass diffused rapidly into the substrate to alter the film composition, but the change in composition itself is found to have no important effect on the modification of the PT films.

The substrates do have a remarkable effect on the modification of the coated films. Typical examples of XRD patterns of the PLZT films on various substrates are shown in Fig. 6. Very broad peaks in this figure can be assigned to the pyrochlore. On glass substrates the pyrochlore is mainly formed, but when the glass substrates were coated in advance with very thin crystalline TiO_2 or ZrO_2 films (about 40 to 60 nm thick) [13, 14], perovskite preferentially grew. On single-crystal alumina, selective perovskite growth was observed. Therefore, it can be presumed that some expitaxial effects controlled the modification of the films.

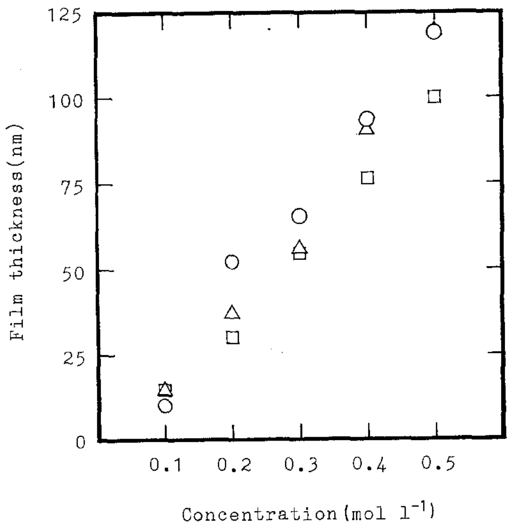

Figure 5 The relationship between the concentration of the dip solution and the thickness of PT films coated by the solution at 500° C. (○) Density, (△) SEM, (□) Talysurf.

In order to confirm the epitaxial effect of the substrate, the XRD patterns of PT films grown at 700° C on various single-crystal plates including MgO, TiO_2, ZrO_2 (YSZ), $SrTiO_3$ were examined, and are shown in Fig. 7. The lattice constants of the substrates and of perovskite and pyrochlore PT are shown in Table I. It was found that on $SrTiO_3$, strongly *c*-axis-oriented films grew, different from the films on other plates. The lattice constant of cubic $SrTiO_3$ ($a = 0.3905$ nm) is very close to the *a*-axis spacing of tetragonal PT ($a = 0.3899$ nm, $c = 0.41532$ nm): the misfit is smaller than 0.2%. The films on MgO had a tendency to peel off, and showed no strong orientation (partly oriented to the *c*-axis rather than the *a*-axis), although it has been reported that strongly *c*-axis-oriented PT films grew on the MgO by r.f. sputtering [5]. The films

TABLE I The lattice constants of PT and single-crystal substrate used

Compound	Crystal form	Lattice Constant	
		a (nm)	*c* (nm)
$PbTiO_3$			
(perovskite)	Tetragonal	0.3899	0.415 32
(pyrochlore)	Cubic	1.040	
Al_2O_3	Hexagonal	0.4758	1.2991
MgO	Cubic	0.4213	
TiO_2 (rutile)	Tetragonal	0.459 33	0.295 92
ZrO_2 (YSZ)	Cubic	0.515	
$SrTiO_3$	Cubic	0.3905	
Platinum	Cubic	0.392 31	

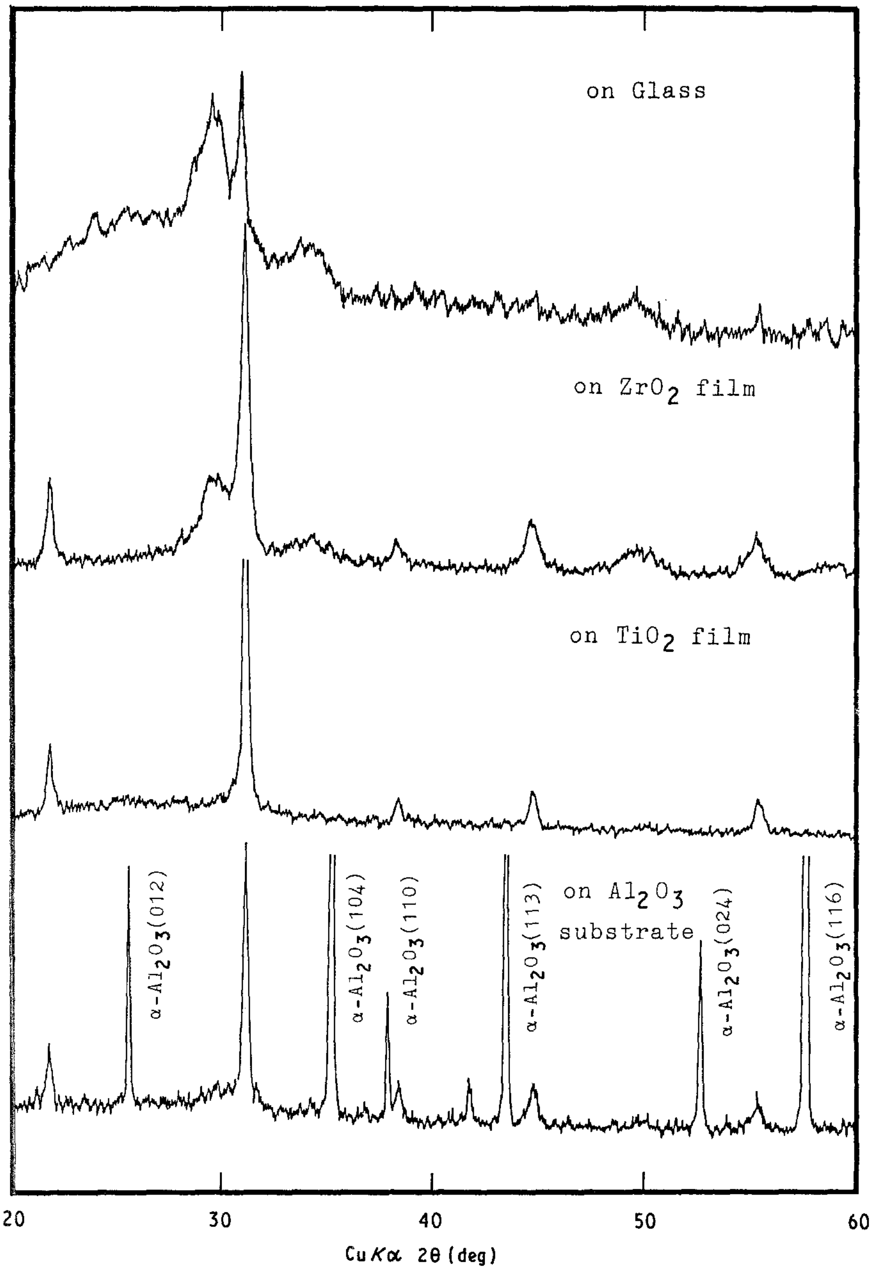

Figure 6 XRD patterns of $Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$ films coated on various substrates at 500° C.

grown at 500° C showed no particular orientation in all cases.

The variation of XRD patterns of PT powders derived from the PT gels with heating temperature is shown in Fig. 8. The cubic pattern observed at 300° C was not assigned to the pyrochlore but to metallic lead, which probably formed due to a reductive thermal decomposition of a lead compound, say alkoxide, under oxygen deficient conditions in the bulk interior. The metallic lead was subsequently oxidized to lead oxide at 400° C, and the oxide reacted to yield the perovskite PT. Throughout the temperature region investigated no pyrochlore was observed. Therefore, pyrochlore formation is considered to be restricted to the case of a film coating especially on the amorphous plates. Fine crystallites of lead oxides, formed as the intermediates in the gel powder, would exert some epitaxial effect on the preferential perovskite formation.

These findings can be summarized as follows.

1. Around 500° C, pyrochlore sometimes grows together with perovskite, but above 550° C only perovskite is formed.
2. Pyrochlore formation proceeds if very thin films are coated on amorphous substrates around 500° C.
3. Crystalline substrates accelerate the growth of perovskite by some epitaxial effect. Due to this, a highly oriented film grows on single-crystal $SrTiO_3$ plates.
4. No pyrochlore formation occurred in powders, and the fluctuation in stoichiometry has no effect on the modifications.

These findings indicate the importance of a thin-film effect, namely the effect of surface energy. This effect is thought to be very strong. It is true that the crystalline substrates accelerate the perovskite formation, but the pyrochlore forms on a platinum plate in the case of very thin films below 100 nm, as shown in Fig. 9. It is well known that the surface energy plays an important role in the modification and properties of the crystals. In this study it was first thought that the surface energy effect may be responsible for the pyrochlore formation. However, perovskite has a higher density than pyrochlore, so it is unlikely that the lower density form (pyrochlore) can be stabilized by a large surface energy, that is the morphology of a

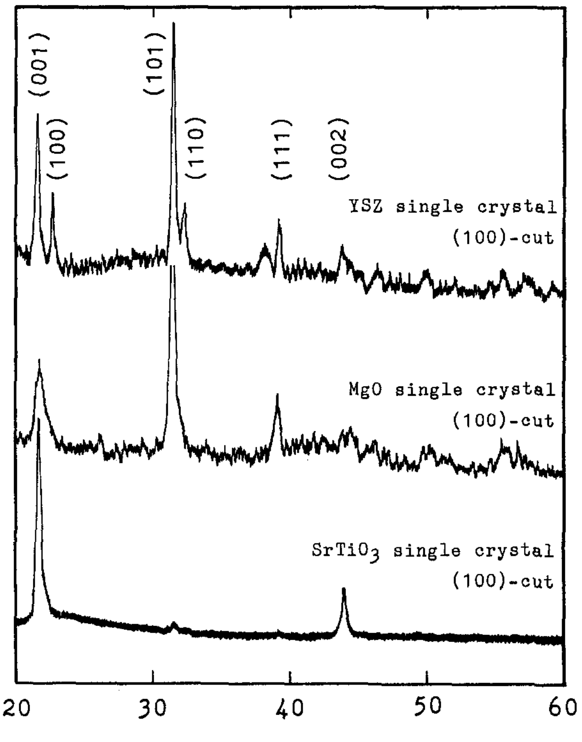

Figure 7 Examples of XRD patterns of PT films grown on single crystal plates of YSZ, MgO and $SrTiO_3$ at 700°C. PT = 0.2 M, R = 1, W = 3.

very thin film. Therefore, there must exist another important factor to be taken into account. We consider this to be the effect of the structure of the polymer species contained in the solution. The alignment of metallic atoms in the polymer species can define, at least partly, the structure of the gel films derived, and hence the structure of the final products, the oxides. It is presumed that the structure of thinner gel films is more strictly defined by the structure of the polymer species in the sol, because gelation begins from the film surface. If this assumption is true, the composition of the solution will affect the modifications of the PT films. In order to confirm this, the effect of the composition of the solution on the modification of the films was investigated.

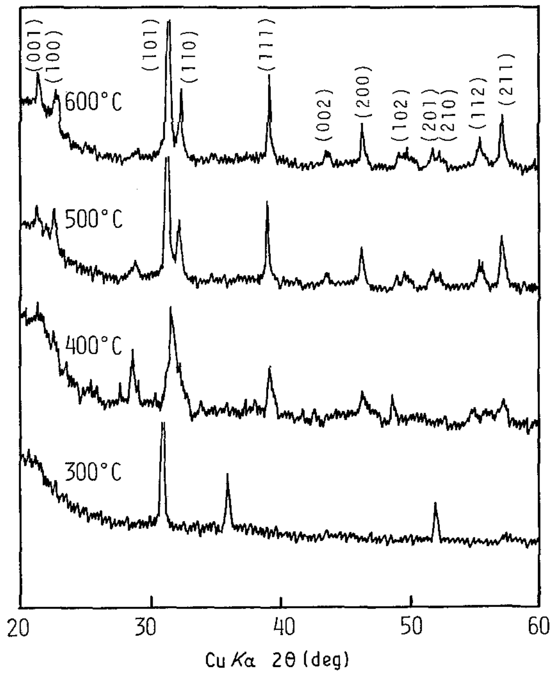

Figure 8 Variation of XRD of PT gels with heating temperatures.

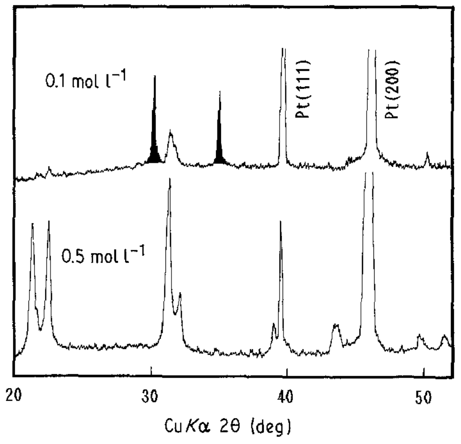

Figure 9 XRD of PT films formed on a platinum plate at 500° C using 0.1 M PT solution. R = 1, W = 3.

In Fig. 10 the effect of the solvent is shown, where titanium tetraisopropoxide was used as the titanium source of PT. The concentration of PT was 0.2 M. The solvent may vary in the degree of association of the alkoxides, thus affecting the structure of the polymer species in the solution. Fig. 10 suggests that the pyrochlore formation was remarkable in lower alcohols, such as methanol, compared to higher ones, such as tert-butanol. When the ethoxide was used as the titanium source in place of the isopropoxide, a similar trend was observed. However, these results can be easily explained by the effect of solvent viscosity, rather than the structure of the chemical species. Lower alcoholic solvents have lower viscosities, and hence they can give thinner films because the viscosity is known to affect the thickness of dip-coated films in

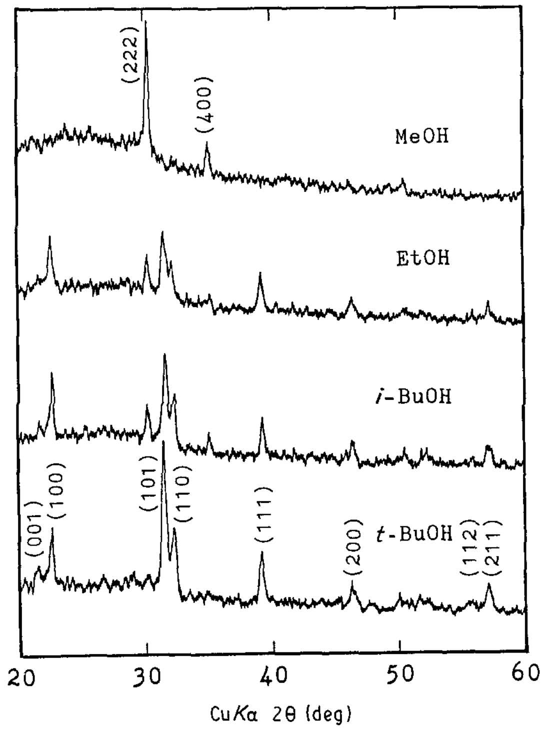

Figure 10 Effect of the solvent for the dip solution on the modifications of PT films. PT = 0.2 M, R = 1, W = 3, Ti source = TTIP.

a square root relationship [13, 15]. As a result, it can be concluded that the effect of film thickness itself must affect the modifications. Fig. 10, however, suggests that the orientation of the PT crystals in the films is different in different solvents, and in ethanol, strongly *a*-axis-oriented perovskite is formed, further suggesting the complex effects of solvents.

Here the dip-coating process of PT, PZT, etc., must be mentioned. As shown in Fig. 8, metallic lead was separated out during the heat-treatment of the gels, suggesting that the segregation of lead species was unavoidable during the heat-treatment of the PT gels, especially in the bulk state, in spite of the precautions taken during preparation of the homogeneous sol. In this sense, therefore, the sol–gel process is not suitable for preparation of monolithic PT and PZT. In film coating, however, the segregation of metallic lead can be avoided by the expected concurrent oxidation of metallic lead due to the rapid oxygen diffusion through the thin film. If the oxidation of metallic lead and the reaction of the resultant lead oxides with titanium species proceeded very smoothly, namely without accumulation of metallic lead and/or lead oxides, the formation of titanates would occur homogeneously. In this case, pyrochlore would grow, which is inherently stable at the temperature concerned (around 500° C). On the other hand, if crystalline intermediates, e.g. lead oxides, were accumulated during heat-treatment, they would force the perovskite to grow by the epitaxial effect. Thick films and gels, we conclude, can produce perovskite by the heterogeneous reaction. If an efficient modifier were added to induce the segregation of metallic lead, only pyrochlore films would be obtained around the critical temperature. The dip-coating method has the merit of yielding perovskite films at temperatures as low as 500° C. Thus, if impurities including carbonaceous compounds were effectively eliminated at low temperatures, the sol–gel process should become very advantageous, although electron spectroscopy for chemical analysis of PT and PZT films suggested the absence of carbon atoms in these films.

4. Conclusion

It was found that the modification of dip-coated PT and PZT films strongly depended on the film thickness and the substrate, as well as on the heat-treatment temperature. Around critical temperatures, 500 to 550° C, metastable paraelectric pyrochlore grows on glass plates (amorphous plates) when the thickness of the coated films produced by one coating cycle was below 100 nm, while ferroelectric perovskite forms on crystalline substrates or when thick films were coated on amorphous plates. The origin of this behaviour was thought to lie in the homogeneous and heterogeneous reaction and the epitaxial effect. The perovskite PT films coated on single-crystal $SrTiO_3$ plates at 700° C were strongly oriented to the *c*-axis.

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