

The effect of PVP on the critical thickness and properties of PLZT ceramic films

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Abstract Increasing the critical thickness (the maximum film thickness of one coating before crack formation) is a key factor for efficiently preparing thick films by sol gel processing. In order to increase the critical thickness of lanthanum doped lead zirconate titanate (PLZT, 9/65/35) films, three types of PVP40000, PVP360000 and PVP630000 (polyvinylpyrrolidone, with the molecular weight of 40000, 360000 and 630000 individually) were used to modify the sol gel processing. Both PVP type and concentration have been found to have significant influence on the critical thickness and crystallization behavior of PLZT films. With increasing the concentration or molecular weight of PVP, the critical thickness increased. But the formation of perovskite was suppressed. PVP360000 was found to be an optimal modifier for preparing PLZT thick films. Crack-free and dense PLZT films with the thickness of 1.33 μm were prepared from PVP360000 modified sols by only three coating. The films have a transparency of about 70% in visible wavelength range and a hysteresis loop with Pr of 3.3 $\mu\text{C}/\text{cm}^2$ and Ec of 40.4 kV/cm. These properties are comparable to that of the non-PVP modified films and the literature data of the films prepared by sol gel processing, MOD and sputtering.

Keywords PLZT · Critical thickness · Formation of perovskite · Ferroelectric

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1 Introduction

For traditional MOE sol-gel processing, the critical thickness of films normally is below 0.1 μm . Repetitive coating can increase the thickness to over 1 μm . But the work is very time-consuming and it is hard to control the film quality. Obviously, increasing the critical thickness is a key factor to improve the quality of thick films and processing efficiency. So far, lots of successful examples have been reported in fabricating PbTiO_3 , $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ and BaTiO_3 thick films. For example, Nimit Sriprang and co-workers reported a triol-based sol-gel route for fabricating crack-free PZT films on platinized substrates with the critical thickness of 0.4 μm [1]. Y. L. Tu et al. have developed a diol sol-gel route to obtain PZT films 0.5–0.9 μm thick by one coating on platinized sapphire and the films of up to 10 μm can be made using multilayer deposition techniques [2]. Recently Hiromitsu Kozuka reported that organic polymers with amide groups could increase the critical thickness [3]. By using such polymer as PVP as a modifier, his group successfully fabricated BaTiO_3 and PZT ceramic films with the critical thickness of 1.2 μm and 0.75 μm respectively [4, 5].

$\text{Pb}_{0.91}\text{La}_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ (PLZT) is an important electrooptic ceramic exhibiting very large electrooptic coefficients [6]. The PLZT films with the thickness in the range of 2–25 μm offer great potential for a variety of devices including optical shutters, modulators and displays [7]. But it is very difficult to obtain transparent PLZT films with such thickness by sol gel route due to porous structure. In the present work, we tried to develop transparent PLZT thick films by employing PVP to modify the sol gel processing.

2 Experimental

The sol was prepared from the starting materials of Zirconium propoxide, Titanium isopropoxide, lead acetate trihydrate and lanthanum nitrate. To investigate the effect of PVP type, PVP40000, PVP360000 and PVP630000 were added to PLZT sol according to the mol ratio of 1.5:1 (PVP monomer:PLZT). To study the effect of PVP concentration, PVP630000 was added to sol according to the mol ratio of 0:1, 0.25:1, 0.5:1, 0.75:1, 1:1 and 1.5:1 (PVP monomer:PLZT) individually. First, zirconium propoxide and titanium isopropoxide were dropped into a solution of acetylacetone and 2-methoxyethanol respectively and then mixed to form a clear solution. The solution was added to the mixture of lead acetate trihydrate and 2-methoxyethanol. After that, lanthanum nitrate was added. Once it dissolved, PVP powder will be dropped to the solution. The PVP modified sol will be refluxed at 60–80°C for 2 h and consequently stored for 24 h before using.

The green PLZT films were coated on glass slide from the sols and heated at 250°C and 550°C for 10 min sequentially. The film thickness was measured by Surface Profiler (Alpha-Step 500, Tencor, USA). To study the crystallization behavior of PLZT, the PLZT films were deposited on ITO coated alumina-silicate glass by spin coating and heated at 250°C and 550°C for 10 min sequentially. After repetitive coating, the samples were finally annealed at 600°C or 650°C for 30 min. Some PLZT powder samples were prepared by drying the sol and annealing at 650°C for 30 min. The crystal phase of PLZT was identified by Rigaku ultima type X-Ray Diffractometer (XRD) with the incident angle of 1°. The Surface morphology of the films was observed using a JEOL JSM-6340F field emission scanning electronic microscope (FESEM). The ferroelectric and dielectric properties were studied by the standard Radiant RT6000HVS type ferroelectric tester and HP 4194A Impedance/Gain Phase Analyzer. The transmittance of samples was measured by the UV-Vis spectrometer (UV-2501PC, Shimadzu, Japan).

3 Results and discussion

3.1 Critical thickness affected by PVP

Figure 1 shows the effects of PVP type on the one-coating thickness of PLZT films. Adding PVP can significantly increase the one-coating thickness of PLZT films. The thickness increased more obviously when PVP360000 and PVP630000 were added in sol and especially when the spin speed is below 1000 rpm. The cross(x) in Fig. 1 is marked as the critical thickness. The critical thickness of the films from different sols is summarized in Table 1. It clearly shows that the critical thickness increased gradually with the molecular

Table 1 Critical thickness (t_c) affected by PVP types

Type	no PVP	40000	360000	630000
t_c (nm)	77.5	217.2	493.1	926.7

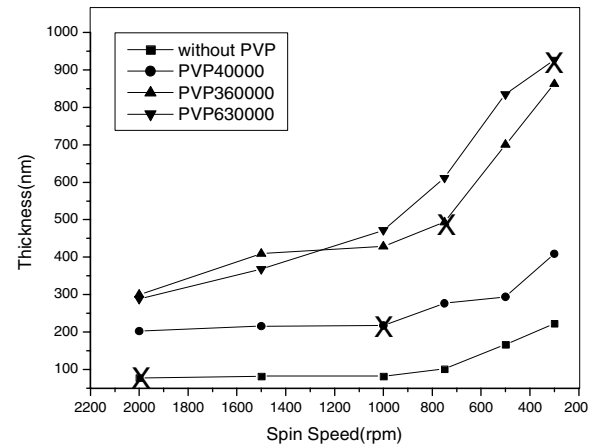


Fig. 1 One-coating thickness of PLZT films affected by PVP types

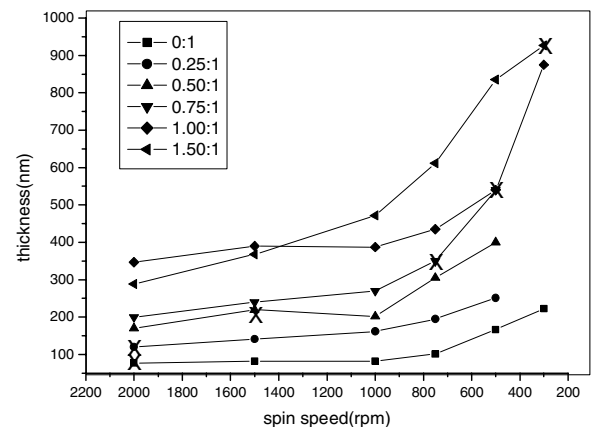


Fig. 2 One-coating thickness of PLZT films affected by the content of PVP630000

weight of PVP increasing from 40000 to 630000. Among the three types of PVP, the samples from the sol modified by PVP630000 have a maximum critical thickness of 926.7 nm.

Since the concentration of PVP directly affects the viscosity of PLZT sol, it is therefore essential to study the relationship between PVP concentration and the critical thickness. As shown in Fig. 2, the one-coating thickness increased with PVP concentration increasing. It is also affected by the spin speed. When the ratio of PVP/PLZT was above 0.75, the thickness increased remarkably with the spin speed decreasing. From Fig. 2, the critical thickness is summarized in Table 2. It is verified that the critical thickness increased with the concentration of PVP630000.

It should be pointed out that although higher critical thickness could be achieved by adding more PVP, too high

Table 2 Critical thickness (t_c) of PLZT films affected by PVP concentration

PVP/PLZT	0:1.0	0.25:1.0	0.5:1.0	0.75:1.0	1.0:1.0	1.5:1.0
t_c (nm)	78.0	120.0	219.3	350.0	540.0	926.7

Table 3 Perovskite volume of PLZT films derive from different PVP type

PVP type	PVP40000	PVP360000	PVP630000
In films % Pe at 600°C	100.00%	90.85%	77.68%
In films % Pe at 650°C	100.00%	96.73%	91.74%

concentration of PVP leads to ununiform surface and poor densification of PLZT films.

3.2 Crystallization behavior of PLZT films affected by PVP

The effect of PVP types on crystallization behavior of PLZT was investigated. PLZT films about 1.30 μm thick were prepared from the three sols with PVP40000, 360000, 630000 individually. The perovskite volumes of the PLZT samples were calculated by the following equation:

$$\%Pe = \frac{I(110)_{Pe}}{I(110)_{Pe} + I(222)_{Py}} \times 100\%$$

where the Pe means the perovskite and Py means the pyrochlore phase. The results are listed in Table 3. It is indicated that the formation of perovskite is suppressed by adding a larger molecular weight of PVP. For the films modified by large molecular weight PVP such as PVP630000 and PVP360000, only 91.74% and 96.73% of perovskite volume can be obtained respectively at 650°C, while pure perovskite phase have been found in the films with PVP40000 at an annealing temperature as low as 600°C.

The effect of PVP630000 concentration on the crystallization behavior of PLZT was also studied in the present work. PLZT dry gels from the sols with PVP monomer/PLZT ratio in the range of 0:1–1.5:1 were annealed at 650°C for 30 min. The perovskite volumes of the samples were calculated and shown in Fig. 3. From Fig. 3, PVP concentration significantly influenced the perovskite transformation. For the PLZT dry gels with low content of PVP, it is easy to transform to perovskite phase completely. But when the PVP content was above 0.5 times of the PLZT mol concentration, perovskite volume dropped down with the PVP concentration increasing. In the films with PLZT:PVP = 1:1.5, only 92.6% of perovskite volume was obtained.

3.3 Morphology, electric and optical properties of PLZT films modified by PVP

In the case of above results regarding the effect of PVP types on the critical thickness and phase transformation,

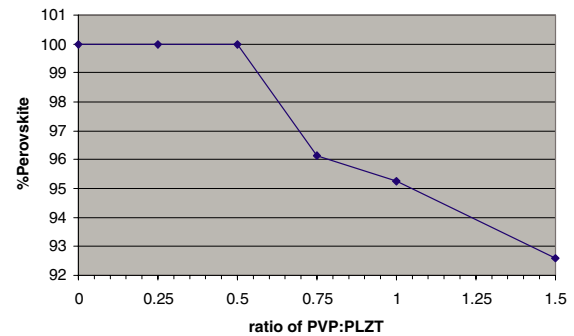


Fig. 3 Perovskite volume of PLZT powder with different PVP concentration

PVP360000 should be an optimal modifier among the three types of PVP, since it produces a comparatively higher critical thickness and good crystallization. Therefore the further studies on the optical and electrical properties are based on the PLZT films derived from the PVP360000 modified sol.

A 1.33 μm -thick sample was prepared from the sol with the ratio of 1.5:1 (PVP360000 monomer/PLZT) by three coating, and annealed at 650°C for 30 min. Figure 4 shows the morphology of the sample. The films are dense and crack-free, with average grain size of about 66.6 nm. The P-E hysteresis loop of the sample was measured under 18 V, as shown in Fig. 5. The remanent polarization and the coercive field are 3.3 $\mu\text{C}/\text{cm}^2$ and 40.4 kV/cm respectively. The dielectric loss and relative dielectric constant at 10 kHz are 0.092 and 263.995 individually. Besides, the sample has a transmittance of about 70% in the wavelength range of above 600 nm, as shown in Fig. 6.

The remanent polarization, coercive field, dielectric constant and transmittance of the sample are listed in Table 4, together with that of the sample without PVP360000 modification and literature data for comparison. It is indicated that the ferroelectric, dielectric properties of the PVP360000 modified PLZT films are comparable to those of the films without PVP360000 modification, although adding PVP suppresses the perovskite transformation (Table 3). And furthermore, the PVP360000 modified films have higher transmittance (70%). This is attributed to that adding PVP induces dense and crack-free PLZT films with high critical thickness so

Table 4 Electric and optical properties of the PLZT (9/65/35) films with PVP360000 modification, without PVP modification and some literature data

Processing	Dielectric constant (10 k)	Pr ($\mu\text{C}/\text{cm}^2$)	Ec (kV/cm)	Transparency (632 nm) (in visible wavelength)
PVP360000 modified	264	3.3	40.4	70%
Non-PVP modified	387	2.1	23.2	50%
Sol gel (0.5 μm) [8]	–	4.8	75	60–70%
MOD (0.6 μm) [9]	–	8.8	40	70%
sputtering(0.5 μm , 8/65/35) [10]	500	4.2	–	82%
Bulk [11, 12]	6000	1.6	1.1	60%

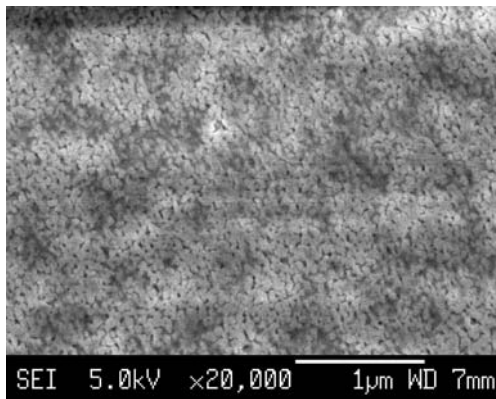


Fig. 4 Morphology of PLZT films modified by PVP360000

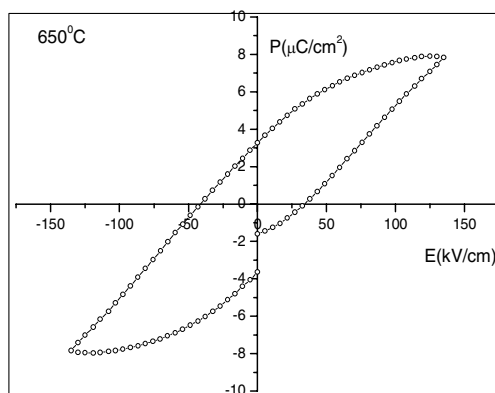


Fig. 5 P-E hysteresis loops for the PLZT films modified by PVP360000

that it only need three coating to get the 1.33 μm -thick films. For the films without PVP modification, it need 13 coating to get the similar thickness and there is some cracks in the films after annealing at a low temperature 600°C for 30 min. So there is reflection loss in the interface of the multilayer structure and the cracks, inducing a lower transmittance.

The electrical and optical properties of the PVP360000 modified PLZT films are also comparable to the literature data of the PLZT films prepared by sol gel processing, MOD, and sputtering. Besides, the remanent polarization and transmittance of the PLZT films are close to that of bulk PLZT, but the films have significantly lower dielectric constant and higher coercive field than that of the bulk PLZT, which may

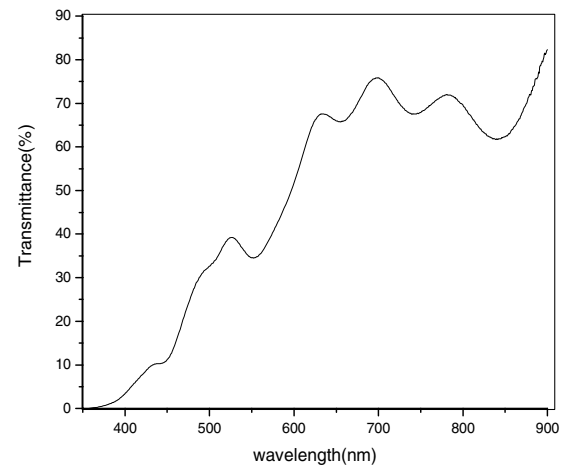


Fig. 6 Optical transmission spectrum for the PLZT thin films modified by PVP360000

be caused by the voids in the film structure and the smaller grain size.

4 Conclusion

In summary, Both PVP type and concentration have been found to have significant influence on the critical thickness and crystallization behavior of PLZT films. With increasing the concentration or molecular weight of PVP, the critical thickness increased. But the formation of perovskite was suppressed. PVP360000 was found to be an optimal modifier for preparing PLZT thick films. Crack-free and dense PLZT films with the thickness of 1.33 μm were prepared from PVP360000 modified sols by three coating. The dielectric, ferroelectric and optical properties of the films are comparable to that of the non-PVP modified films and the literature data of the films prepared by sol gel processing, MOD and sputtering.

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