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Electrical and optical properties of PLZT thin films on ITO coated glass by sol-gel processing

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Sol-gel processed PLZT thin films were fabricated on ITO-coated glass substrates with RTA (rapid thermal annealing). The electrical and optical properties such as hysteresis curves, dielectric constant, dielectric loss and optical transmittance of thin films were investigated. The PLZT thin films were crystallized to the perovskite structure by RTA at 750 °C for 5 min. As the La percentage was increased, the dielectric constant increased, and that of 9/65/35 PLZT thin film was 1750. The coercive field and remnant polarization decreased with La increase from 33.82 kV/cm to 14.71 kV/cm and from 39.26 μC/cm^2 to 9.57 μC/cm^2 respectively. As the Zr percentage increased at 2% La, the coercive field decreased from 52.94 kV/cm to 30 kV/cm, but the remnant polarization increased from 22.74 μC/cm^2 to 50.75 μC/cm^2, and the dielectric constant had a maximum value of 1269 at 2/55/45 composition. The optical transmittance was increased as La percentage increased but was decreased as the annealing temperature increased. © *2000 Kluwer Academic Publishers*

1. Introduction

Since, lanthanum modified lead zircornate titanate, PLZT bulk ceramics were developed by Haertling and Land in the early 1970s, PLZTs have been most widely known for their high optical transparency, broad category of compositions and various electro-optic coefficients. PLZTs are desirable candidates for electro-optic applications such as light shutters, modulators, color filters, memories and image storage devices [1–3]. But these are weighed against the disadvantages of high operating voltage, incompatibility with IC's, high cost, and limited size availability. In order to resolve these disadvantages, recent research on PLZT has changed its focus from the bulk materials to thin films. Early work on fabrication of PLZT thin films was mainly based on vacuum deposition techniques such as ion beam deposition and sputtering [4, 5]. However, problems of poor stoichiometric control and complex sets of deposition parameters in vacuum techniques have hindered the deposition of device quality films. In recent years there has been much interest in fabrication of oxide films using sol-gel techniques [6, 7]. Sol-gel processing has advantages in better stoichiometric control and film homogeneity, lower processing temperatures, easy composition control, and lower cost.

Thin films deposited on indium tin oxide (ITO) coated glass substrates, cannot be heated to high temperatures due to possible degradation of the substrate. This makes it difficult to anneal thin films to the pure perovskite phase. Recently, rapid thermal annealing (RTA) has been found to be an excellent method to make perovskite phase in thin films [8, 9].

In this study, various PLZT thin films were prepared by sol-gel processing. The compositions studied were $Pb_{1-x}La_xZr_{0.65}Ti_{0.35}O_3$, where x was 0.02, 0.04, 0.06, 0.08, 0.09 and 2/Zr/Ti where Zr/Ti was varied from 20/80 to 80/20. These films were deposited on ITO-coated glass by spin coating and were annealed by rapid thermal annealing (RTA) to measure electrical and optical properties.

2. Experiment

PLZT stock solutions were prepared by modified sol-gel processing suggested by Sayer et al. [10] and stoichiometrically combined based on the formula $pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ [1]. 10 mol% excess lead acetate was added to compensate Pb loss in the form of PbO vapor during annealing process. Lead acetate and lanthanum acetate was dissolved into acetic acid at 95 °C for 1 hour. Zirconium *n*-propoxide and titanium iso-propoxide were mixed with acetic acid and *n*-propanol at 40 °C for 1 hour to insure homogeneity of the mixture.

The two solutions were mixed at 40 °C for 30 min and 2 mol of H_2O was added for hydrolysis. Acetic acid (0.2 mol) was then added to the solution to control the hydrolysis process, and ethylene glycol was added to improve the surface flatness and to avoid cracks on the film [11]. The concentration of solution was adjusted to 0.5 M by adding a proper amount of *n*-propanol.

The prepared PLZT stock solutions were aged over 24 hours before use. Glasses with 100 nm of ITO were used for fabricating transparent PLZT thin films. Prior to film deposition the substrates were cleaned with commercial detergent to remove dirt and oil, then thoroughly rinsed.

PLZT stock solutions were deposited by a spin coater at 5000 rpm, for 30 sec on ITO-coated glass and dried on a hot plate at 400 °C for 10 min to decompose the organics. This procedure was repeated 10 times in order to obtain a film thickness of approximately 1.7 μm. All of the films in this study were in this thickness range. Crystallization of the amorphous film was carried out by RTA.

X-ray diffraction (XRD) was used for studying the effect of RTA temperature on the PLZT thin films. RTA processing of PLZT thin films was carried out from 650 °C to 800 °C for 5 min and from 30 sec to 5 min at 750 °C, PLZT thin films were also crystallized at 750 °C for 5 min.

Electrical properties measurements were carried out after evaporating 250 μm diameter Ag top electrodes. Hysteresis was measured using a Sawyer-Tower circuit with a 47 nF standard capacitor and applying a ±30 V peak a.c. test signal at 1 kHz. Dielectric constant and dielectric loss were measured by a HP 4263 LCR meter at 1kHz with an a.c. test voltage of 20 mV with no d.c. bias. The optical transmittances were measured by a SHIMADZU UV-160A UV spectrophotometer with a wave length of 300–800 nm.

3. Result and discussion

XRD of 9/65/35 PLZT thin film annealing for 5 min at different annealing temperature are shown in Fig. 1. The PLZT thin film annealed at 650 °C began to be crystallized, but consisted of mainly pyrochlore phase. The film annealed at 700 °C consisted of perovskite phase and pyrochlore phase. The films annealed at 750 °C consisted of perovskite phase and was completely crystallized. There was no difference between 750 °C and 800 °C. Fig. 2 shows the XRD of 9/65/35 PLZT thin film annealing at different annealing time for 750 °C in Fig. 2. The PLZT thin film annealed for 30 sec consisted of mainly pyrochlore phase. For 1 and 3 min, the thin film consisted of mainly perovskite phase and a few of pyrochlore phase. For 5 min the films consisted of perovskite phase. PLZT thin films prepared by sol-gel processing were fully crystallized by RTA at 750 °C for 5 min.

The electrical properties are listed for PLZT thin films in Table I including dielectric constants and dissipation factors as well as coercive field and remnant polarization from hysteresis loops. Fig. 3 shows the dielectric constant and dielectric loss according to composition. For X/65/35 compositions, as expected,

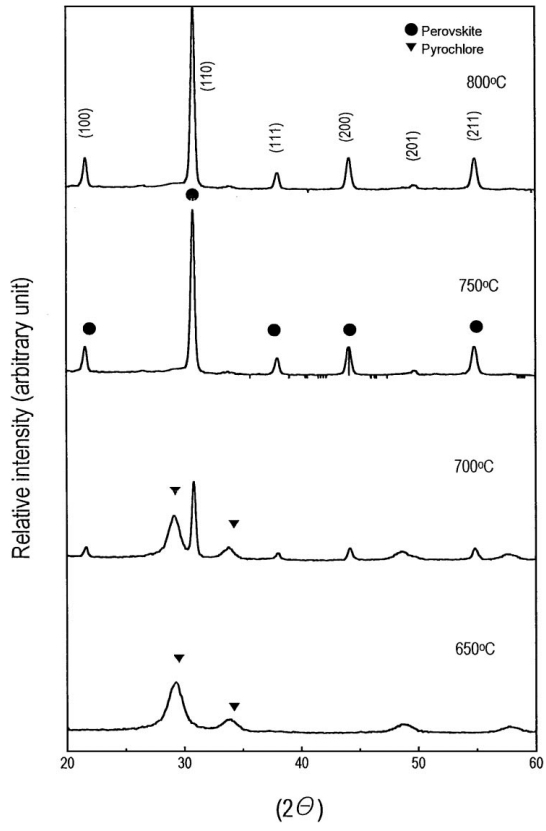


Figure 1 XRD analysis of 9/65/35 composition with annealing temperature. The RTA time was 5 min.

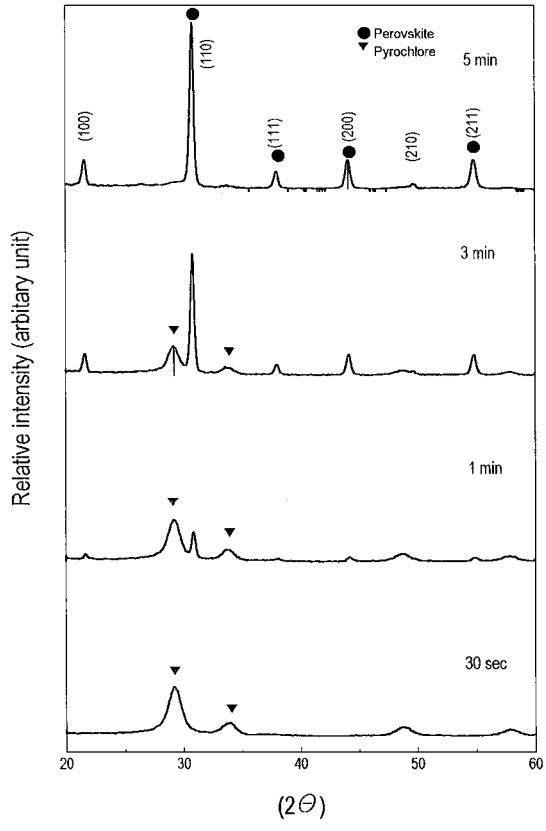


Figure 2 XRD analysis of 9/65/35 composition with annealing time at RTA temperature at 750 °C.

dielectric constant increased with increasing La percentage and showed maximum value of 1750 at 9/65/35 composition at the paraelectric phase boundary. For the 2% La composition, the dielectric constant showed a

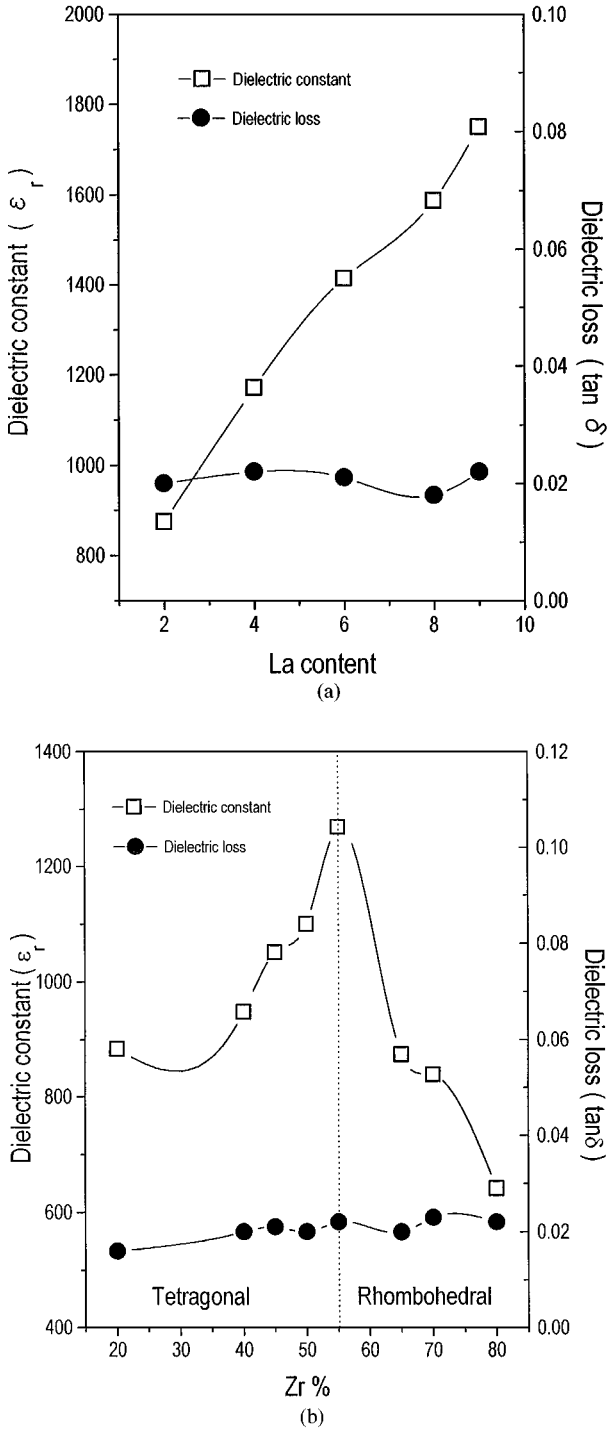


Figure 3 (a) Dielectric constant and dielectric loss with La percentage in X/65/35. Measurements were done in an HP 4263 LCR meter at a frequency of 1 kHz with test voltage of 20 mV with d.c. bias. (b) Dielectric constant and dielectric loss with Zr/Ti ratio for 2% lanthanum. Measurements were done in an HP 4263 LCR meter at a frequency of 1 kHz with test voltage of 20 mV with no d.c. bias.

maximum value of 1269 at the 2/55/45 composition indicating the existence of a MPB near this composition. However dielectric losses remained nearly constant over the range.

Fig. 4 shows the coercive field and remnant polarization of PLZT thin films with varying La percentage measured from hysteresis. Coercive field and remnant polarization decreased as La percentage increased. As Zr percentage increased with 2% La, coercive field was decreased but remnant polarization was increased. This

TABLE I Dielectric and ferroelectric properties of PLZT thin films at room temperature

Composition	*K*	tan δ	Ec	Pr
2/20/80	884	0.016	52.94	22.74
2/40/60	948	0.020	51.47	23.94
2/45/55	1051	0.021	50.00	28.72
2/50/50	1100	0.020	47.06	31.60
2/55/45	1269	0.022	40.00	32.55
2/65/35	875	0.020	33.82	39.26
2/70/30	839	0.023	30.00	50.75
2/80/20	642	0.022	32.29	50.75
4/65/35	1172	0.022	28.24	23.94
6/65/35	1415	0.021	26.47	19.15
8/65/35	1587	0.018	18.24	15.32
9/65/35	1750	0.022	14.71	9.57

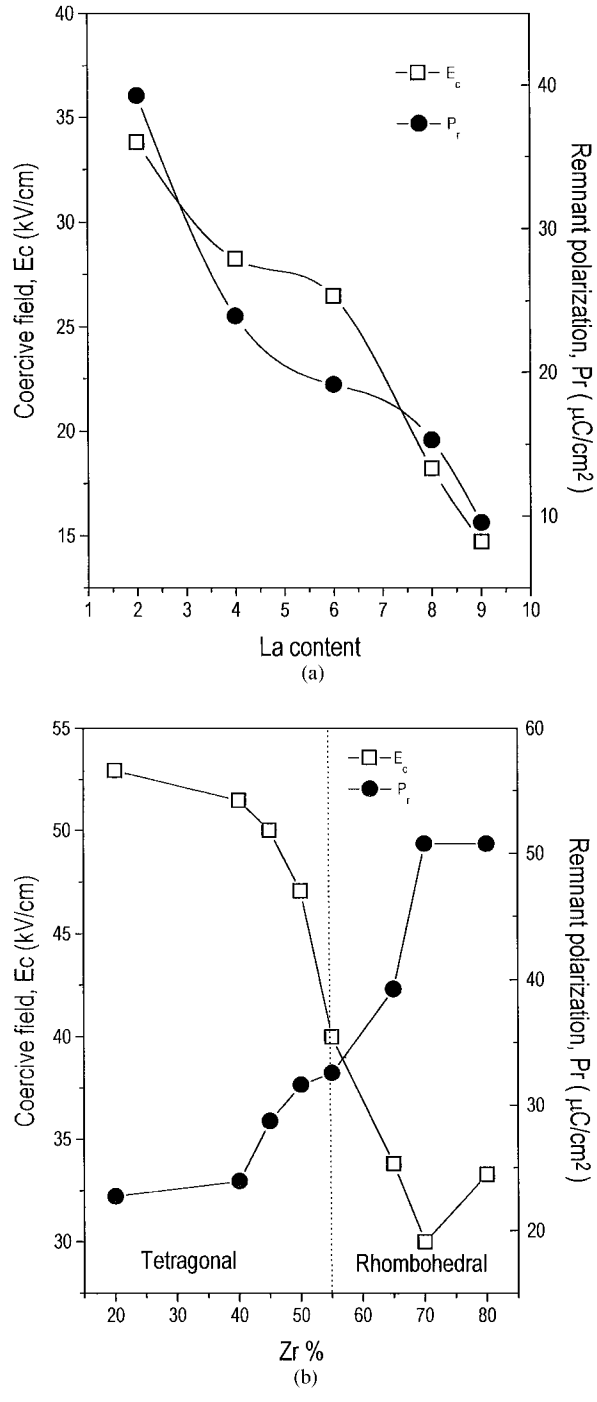
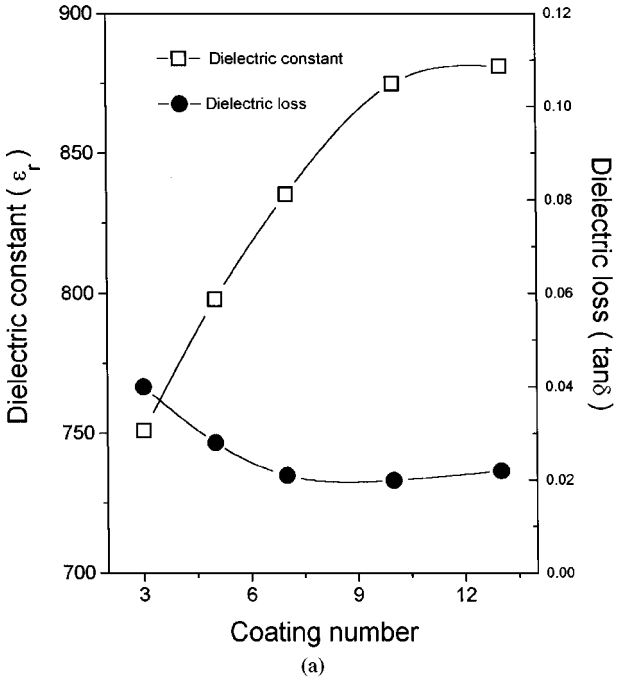


Figure 4 (a) Coercive field and remnant polarization with La percentage in X/65/35 composition. (b) Coercive field and remnant polarization with Zr/Ti ration changed in 2% La.

behavior is similar to bulk PLZT ceramics [1]. Coercive field was higher and remnant polarization was lower for thin films than those of bulk ceramics [12]. These phenomena were attributed to the clamping effects at the films and substrate interface, and the residual stresses and small grain size in thin films [13, 14].

Due to these effects the dielectric constant, coervice field and remnant polarization were found to be apparently dependent on film thickness. It is expected that the clamping effects from the substrate will be reduced as film thickness increased, but the effect cannot be removed completely. Fig. 5 shows the dielectric constant, coercive field and remnant polarization as a function of film thickness. The dielectric constant and remnant polarization increased and the coercive field and dielectric loss decreased as film thickness increased. These can be explained by low permittivity thin layers between electrode and thin films. As thickness increased, the effect of low permittivity thin layers at the surface and electrode interface and stress in the thicker layers was reduced.

The most outstanding feature of PLZT materials is their high optical transparency. The transparency is a function of La percentage as well as Zr/Ti ratio; the maximum transparency is achieved along the ferroelectric and paraelectric phase boundary. Fig. 6 shows optical transmittance of 2/65/35 PLZT thin films as a function of annealing temperature. As the annealing temperature increased optical transmittance was decreased because the thin films annealed at 650 °C and 700 °C consisted of mainly pyrochlore structure which is centrosymmetric [15]. But the thin films annealed at 750 °C were crystallized in the perovskite phase and scattered the light, reducing the transmittance. In Fig. 7, optical transmittance increased as La percentage increased. Because the crystallographic structure was changed from rhombohedral to pseudocubic structure as the amount of La percentage increased and therefore, optical isotropy was increased and optical transmittance increased. But because of small grain size of the thin films, as wave length increased, light scattering was increased in grain boundary and therefore the effect of optical isotropy was decreased. The absorption edge for thin film PLZT was 340 nm compared to that of bulk PLZT at 370 nm.



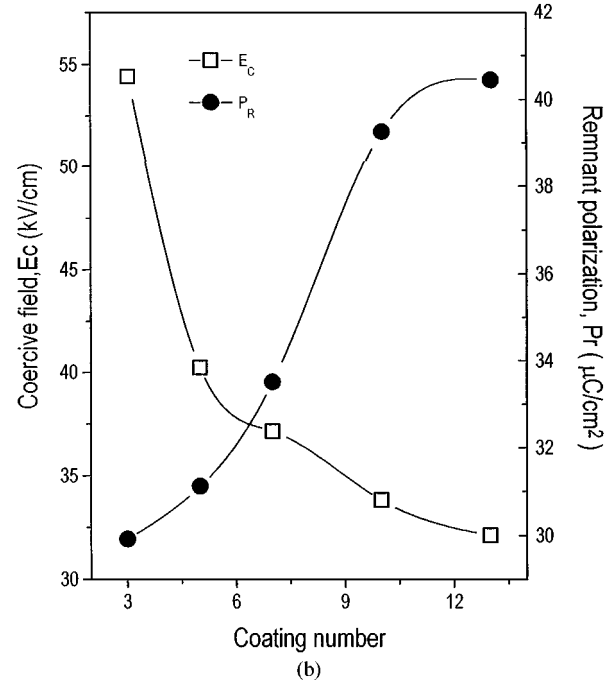


Figure 5 (a) Dielectric constant and dielectric loss of 2/65/35 composition with thickness. Thickness for 10 coating layer in 1.7 μm. The thickness change was proportioned to the number of coatings based on measurement of 3, 5, 10 layers. (b) Coercive field and remnant polarization of 2/65/35 composition with thickness.

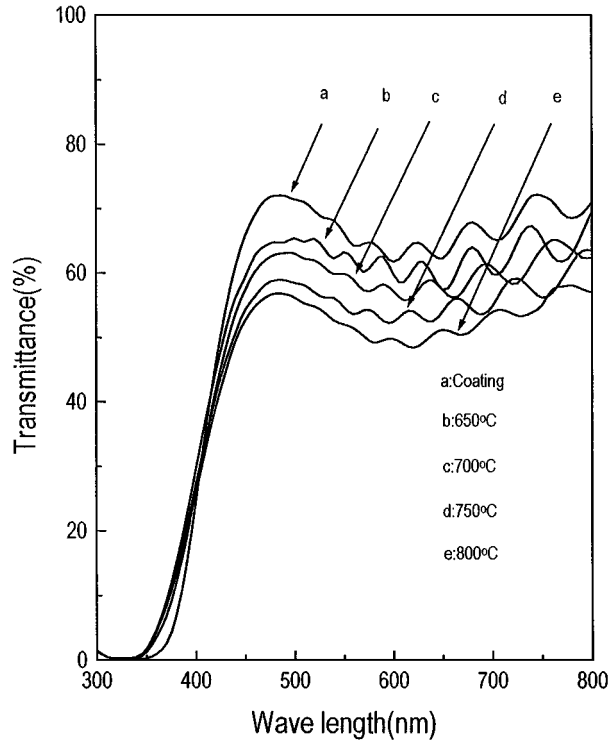


Figure 6 Optical transmittance of 2/65/35 composition with annealing temperature.

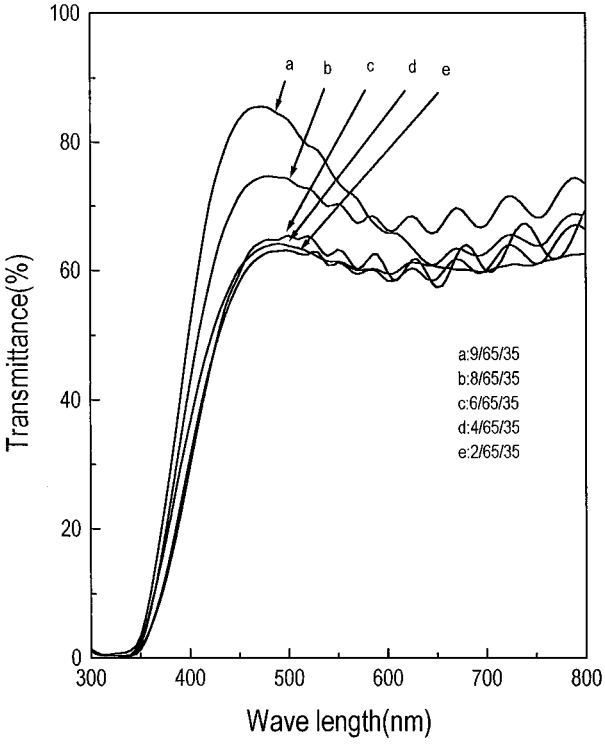


Figure 7 Optical transmittance with La percentage in X/65/35 composition.

4. Conclusion

PLZT thin films prepared by sol-gel processing can be crystallized as perovskite by RTA at 750 °C for 5 min. For X/65/35 composition, dielectric constant of the thin films increased as La percentage increased. Although the PLZT thin films experienced narrowing of their hysteresis loops with increased La percentage, coercive field and remnant polarization were higher for thin films than those for bulk ceramics because of small grains, the clamping effect and the stress in the films. Optical transmittance increased as La percentage increased and was about 70% in the slim loop ferroelectric region. For composition with varying Zr/Ti ratio with 2% La, dielectric constant was maximum at 2/55/45 composition. As Zr percentage increased, coercive field was decreased but remnant polarization increased.

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