ISSN 1996-3343

Asian Journal of Applied Sciences

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Asian Journal of Applied Sciences 7 (8): 713-720, 2014
ISSN 1996-3343 / DOI: 10.3923/ajaps.2014.713.720

Effect of Chelating Ligands on Structure and Electrical Properties of Sol-gel Derived PLZT Thin Films

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ABSTRACT
Lanthanum modified lead zirconate titanate (PZT) thin film with molecular formula $Pb_{0.92}La_{0.08}[Zr_{0.52}Ti_{0.48}]_{0.98}O_3$ (PLZT) was prepared by spin coating of sol-gel solution on $Pt/SiO_2/Si$ substrate. Effect of different chelating ligands (Formamide, poly ethylene oxide, ethylene glycol) on phase formation, microstructure and electrical properties of PLZT thin films were studied to improve the quality of the film for MEMS application. The XRD patterns of the thin films revealed single phase formation of PLZT material with varying crystal structures for different chelating ligands. The Atomic Force Microscopy (AFM) images of these thin films showed surface profiles of 7.3 nm for formamide, 3.78 nm for Poly Ethylene Oxide (PEO) and 2.11 nm for Ethylene Glycol (EG). The dielectric and ferroelectric properties of PLZT film prepared with formamide showed higher spontaneous polarization (P_s) (39.68 μC/cm^2), remanent polarization (P_r) (12.09 μC/cm^2), dielectric permittivity (1840) and piezoelectric coefficient d_{33} (415 pm/V) compared to the films prepared with PEO and EG as chelating agents.

Key words: PLZT thin film, sol-gel, chelating ligands, AFM, ferroelectric, piezoelectric

INTRODUCTION
In the past decades, considerable amount of research has been focused on the growth and application of lead zirconate titanate (PZT) based thin films (Polla and Francis, 1998; De Araujo *et al*., 1995). PZT doped with olivalent compound inherits excellent piezoelectric properties. Substitution of lanthanum for lead (PLZT) in these materials changes their macroscopic properties from normal ferroelectric to relaxor ferroelectric types. A profound effect of relaxation phenomenon has been observed on properties of PLZT materials. In particular, high values of dielectric permittivity, large remanent polarization and optical transmittance, improved electromechanical and electro-optic coefficients are recorded, which make these materials suitable for various applications such as sensors, capacitors, optoelectronic modulators, etc. (Smolenskii *et al*., 1984; De Araujo *et al*., 1997; Haertling, 1986). It is reported that with the increase in lanthanum concentration (5 to 10 mol %), orientation of x-ray characteristic peak changes from (110) to the (111) resulting slimmer hysteresis loop, low coercive field and less polarization (Es-Souni *et al*., 2001; Kugeler *et al*., 2009). PLZT was first prepared by Budd *et al*. (1985). Later it was synthesized in the form of bulk, thin film and composite (Simoes *et al*., 2001; Dausch and Haertling, 1996; Thomas *et al*., 2003). There are various methods of PZT based thin film fabrications (Sun *et al*., 2001; Yang *et al*., 2000; Brooks *et al*., 1994; Lee and Lee, 2001;

Husmann *et al*., 1997; Kim *et al*., 2001). The sol-gel based thin film have advantage over the other methods of thin film fabrication due to its simplicity, purity, homogeneity, fabrication of large area at low cost, low temperature processing, control of stoichiometry and microstructures (Kuo and Tseng, 1996). Chelating ligands are commonly used in chemical sol preparation as stabilizing agents. It also acts as strong nucleophile to promote the chemical reaction.

In the present investigation, effect of different chelating ligands on microstructure and texture (orientation) of PLZT thin films has been studied for the improvement of ferroelectric and piezoelectric properties. It was recognized that the PLZT thin films prepared with different ligands exhibit interesting physical and electrical properties.

MATERIALS AND METHODS

Materials: The starting materials used for the preparation of La-modified PZT (PLZT) thin films of molecular formula $Pb_{0.92}La_{0.08}(Zr_{0.52}Ti_{0.48})_{0.98}O_3$ were lead acetate trihydrade (99%, Loba Chemie, India), lanthanum acetate (99% pure, Loba Chemie, India), titanium isopropoxide (97+%, Alfa Aesar, Ward hill, MA 01835), zirconium n-propoxide (97+% pure, Alfa Aesar, Ward hill, MA 01835), glacial acetic acid (100% GR, Merck, India) as a solvent. Formamide (99% pure, Merck, India), ethylene glycol (99% pure, Merck, India), poly ethylene oxide (99% pure, Loba chemie, India) were used as different chelating ligands.

Method of thin film preparation: 1 M concentrated solution of lead acetate trihydrate and lanthanum acetate were prepared using 2-methoxy ethanol. Zirconium n-propoxide and titanium iso-propoxide which were pre-dissolved in n-propanol were mixed with the starting materials. Acetic acid was added along with water for the weak hydrolysis of the starting materials. Formamide, Ethylene Glycol (EG) and Poly Ethylene Oxide (PEO) were used separately into the stock solution as chelating ligands to promote the chemical reactions. The solution prepared using different ligands showed different viscosity due to the nature of polymeric linkage formed during the reaction. The coated film was pyrolized in two-steps followed by thermal annealing at 650°C for 1 h. Multilayer coating was performed to improve the thickness of the film ~1 μm. As grown PLZT thin films were first characterized by X-Ray Diffraction (XRD) method to confirm the phase formation and orientation. Surface profile was studied by Atomic Force Microscopy (AFM). Electrical contact was given to the film by vacuum evaporation of aluminium following the configuration of Pt/PLZT/Al for electrical characterization. Hysteresis loop (P-E), voltage-capacitance (C-V) characteristics, dielectric constant (ε) and piezocoefficient (d_{33}) of PLZT thin films were measured using thin film analyzer (aixACCT TF analyser 2000, Germany) at 100 Hz frequency.

RESULTS AND DISCUSSION

XRD analysis: Figure 1 shows the XRD patterns of annealed PLZT thin films prepared with different chelating ligands (Formamide, EG, PEO). Here afterwards the films prepared by using formamide will be named PLZTA, Ethylene Glycol (EG) will be named PLZTB and Poly Ethylene Oxide (PEO) will be PLZTC.

The XRD peaks correspond to (100), (110), (111), (200) and (221) crystalline planes were observed in all the three PLZT (A, B, C) films as shown in Fig. 1a-c. It confirms the formation of pure pervoskite phase in PLZT A, B and C. For PLZTA, strong peaks are observed at (100), (111) and (200) (Fig. 1a) among which intensity of (100) peak is highest. In PLZTB and PLZTC, (111) peak is predominant where the intensity of (100) and (200) is 20% of the intensity of (111) peak.

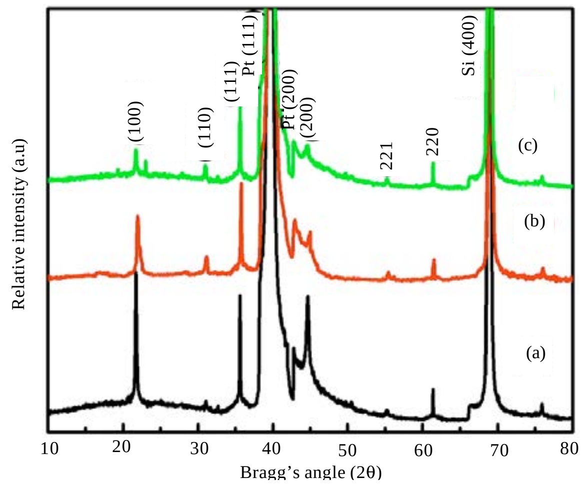

Fig. 1: XRD pattern of PLZT film for different ligands, (a) Formamide, (b) Ethylene glycol and (c) Poly ethylene oxide

Chelating ligand plays an important role for growth and orientation of the film. In PLZTA the prominent orientation along (100) and (111) is associated with the self assembling nature of formamide molecules due to the presence of hetero atoms (C-N, CO). Since oxygen is more electronegative than nitrogen the electron density around oxygen molecules is higher which accelerate the reaction with the electron deficient positive metal ions (Zr^{+4}, Ti^{+4}, Pb^{+2}) in case of formamide. Also, participation of lone pair electrons from neighboring amine (NH_2) group in formamide facilitates the reaction with highly positive metal ions by making the oxygen molecule strong nucleophile. Thus, formamide helps in building 3 dimensional linkages between Pb-O-Zr, Ti. When PbO acts as nucleation centre the crystal growth happens along (100). Formamide ligand makes the molecules to self-assemble during processing and annealing by aiding flexibility to the linkage and allow the crystal to grow along (100) and (111) plane. In case of PLZTB and PLZTC film the predominant peak along (111) is due to the existence of homo atoms (C-O, C-O) in PEO and EG with equal electro negativity which renders rigid C-C bond. This imparts epitaxial growth which is seen here along Pt (111).

There is also a chance of lead (Pb) diffusion into Platinum (Pt) during rapid thermal annealing of PLZT film which forms intermediate transient phase of Pt_3Pb. (111) orientation of PLZTB and PLZTC film is due to Pt_3Pb which acts as nucleation centre and facilitates the growth of PLZTB and PLZTC along (111) direction (Wu *et al*., 2003) through Pt (111) lattice matching.

Atomic force microscopy: Figure 2 shows AFM micrographs of annealed PLZTA, B and C films. The average roughness observed for film A is 7.3 nm, for film B is 3.78 nm and 2.11 nm for film C. A closed compact network structure is seen from the surface profile of thin film PLZTA (Fig. 2a) which is highly densed.

The enhanced grain growth in film A is due to the use of formamide as a chelating agent which facilitated 3d (three dimensional) linkage as mentioned in the previous section. This 3d growth introduces roughness into the microstructure which has been observed in the surface profile (Fig. 2a) with higher average roughness value. In case of PLZTB and PLZTC the effect of EG and PEO (as chelating ligands) on grain growth is not that obvious. It is seen from Fig. 2b and c that

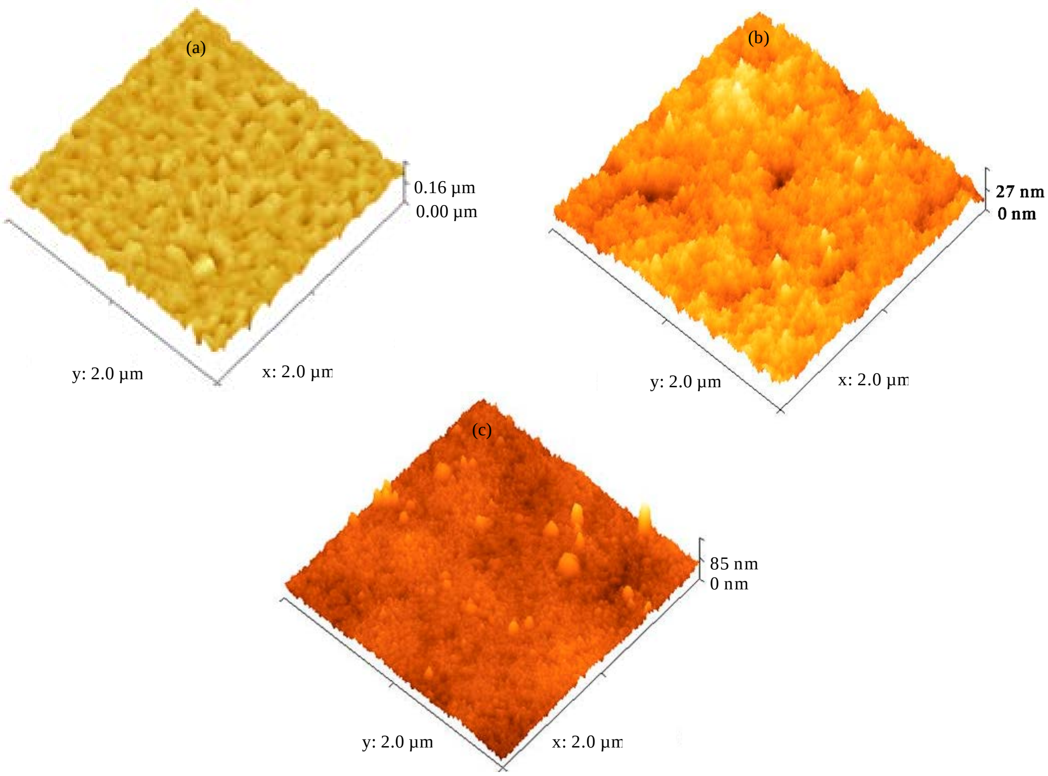

Fig. 2(a-c): Atomic force micrograph for, (a) PLZTA, (b) PLZTB and (c) PLZTC

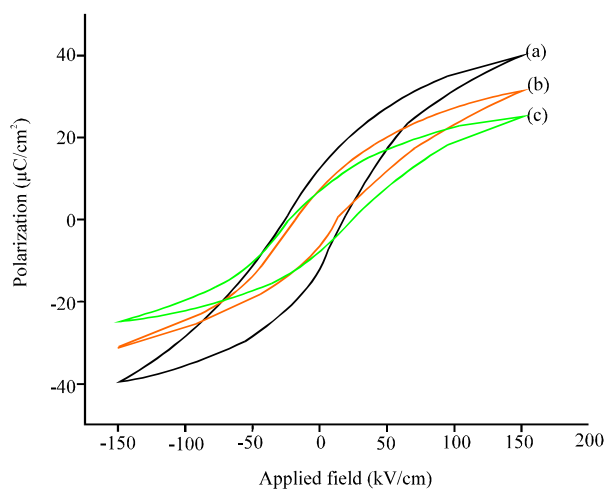

Fig. 3(a-c): P-E hysteresis loop for, (a) PLZTA, (b) PLZTB and (c) PLZTC

EG and PEO based thin films have the smaller grain size along the orientation of the platinum bottom electrode, no compact network structure and less roughness compared to PLZTA. Some porosity is also observed in PLZTC. Hence, it is necessary to totally eliminate pores in order to obtain good quality thin films. The AFM images show that the film A prepared with formamide having good quality compared to film B and C.

P-E hysteresis loop: Figure 3 shows polarization of PLZT thin film A, B and C with different electric fields (P-E loop) at 100 Hz frequency. PE hysteresis loop is an evident of strong ferroelectricity present in these films due to the nature of reversible dipole movement with the applied electric field.

The spontaneous polarization indicates the complete alignment of dipoles with applied electric field whereas the remanent polarization is the polarization retained by the materials after withdrawing the field. The spontaneous polarization (P_{max}) and remanent polarizations (P_r) value was observed higher for PLZTA film and the values are 39.68 and 12.098 μC/cm^2. The value obtained for films PLZTB and C are 30.918, 7.0568 and 24.988, 6.868 μC/cm^2, respectively. The higher P_{max} and P_r of PLZTA film is attributed to the crystal orientation (100), close packed microstructure, enhanced grain growth which facilitates the free domain wall movement. The effect of chelating ligand is found very obvious in controlling the crystal growth with crack free film with quality and improves the electrical properties. It is reported that the crystallographic orientation is also one of the most important factors that determine the electrical properties of PZT and modified films (Du *et al*., 1998; Taylor and Damjanovic, 2000). The remanent polarization values achieved from these films are higher than that of the reported results (Du and Ma, 2006).

The lower remanent as well as spontaneous polarization in film C indicates difficulty in domain switching due to smaller grain size and lower packing density (higher porosity) as seen in microstructure. The coercive field for PLZTA, PLZTB and PLZTC are 21.53, 15.56 and 20.68 kV cm^{-1}, respectively.

C-V curve: Capacitance of these materials are measured following the Metal-Insulator-Metal (M-I-M) structure where the top and bottom electrodes act as metal plates and the capacitance of the material is inversely proportional to the thickness of the film. Figure 4 shows capacitance versus electric field (-150 to +150 kV) of PLZTA, B and C films. All the three curves show butterfly loop

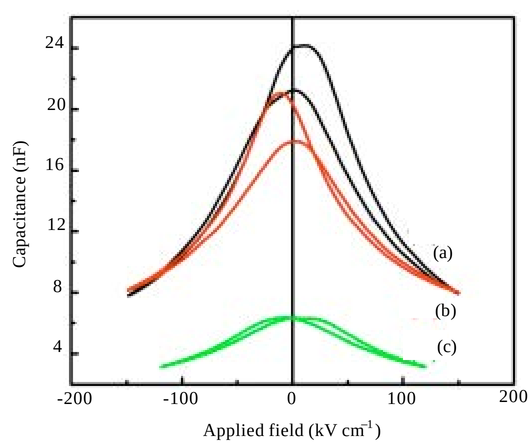

Fig. 4(a-c): C-V curve for, (a) PLZTA, (b) PLZTB and (c) PLZTC which is a characteristic properties of ferroelectric material. The higher capacitance value (24.1 nF) was observed for film A whereas the film B and C showed lower capacitance, i.e., 20.3 nF for film B and 6.3 nF for film C. Less porosity, enhanced grain growth in PLZTA film having higher capacitance value. The low capacitance value in film C is due to porosity and high loss factor.

Dielectric constant: Variation of dielectric constant with electric field for PLZT thin films A, B and C has been studied. The dielectric constant value for film A, B, C were 1840, 1155, 1073 respectively. The higher dielectric constant value of film PLZTA is attributed to the large grain size. Literature also reveals that PZT based films oriented along (100) plane exhibit higher dielectric properties than (111) oriented film. It is previously discussed in the XRD section (Fig. 1) that (100) plane is more dominant in film PLZTA than film B whereas (111) plane was dominant in film C. Thus the improved dielectric property was expected in film A which correlated well with the XRD plot and microstructure.

Piezocoefficient: Figure 5 gives the piezocoefficient (d_{33}) in terms of displacement against applied field in the range -150 to +150 kV cm^{-1}. The piezocoefficient (d_{33}) was found to be higher for PLZTA

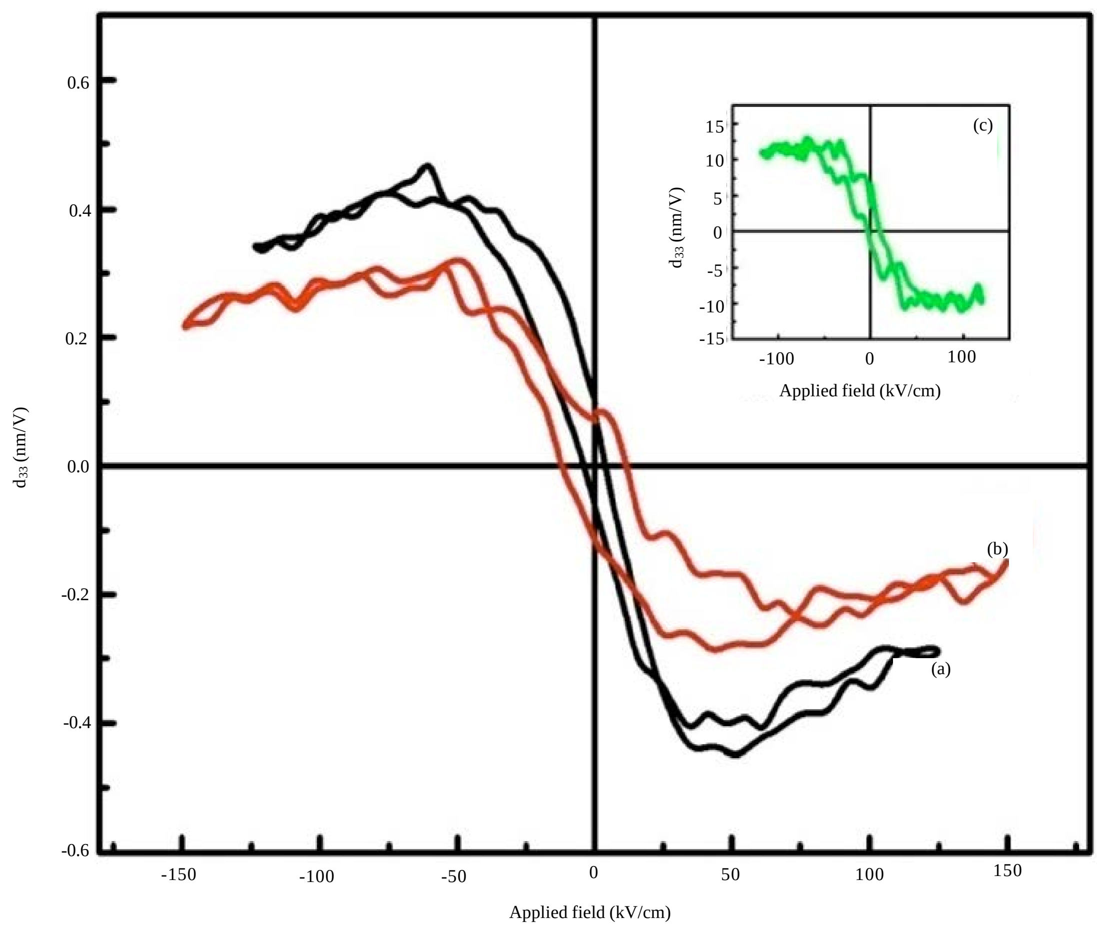

Fig. 5(a-c): Piezocoefficient d_{33} for, (a) PLZTA, (b) PLZTB and (c) PLZTC

(415 pm/V) and the low for PLZTB (280 pm/V), PLZTC(15 pm/V). The high piezocoefficient in film PLZTA is due to the directional growth of the film along (100) and the low value of PLZTC is associate with its orientation along (111). Similar results have also been reported earlier (Du *et al.*, 1998; Muralt, 2000; Park *et al.*, 2005). Domain stability of (100) orientation renders the high d_{33} value (Izyumskaya *et al.*, 2007). The lower d_{33} of PLZTC film is due to the smaller crystallites.

CONCLUSION

PLZT thin films were prepared by spin coating of chemical sol on Pt/SiO_2/Si substrate. Here, different chelating ligands (formamide, EG and PEO) were used in the preparation of sol-gel solutions keeping the other process conditions invariable to study the effect of these ligands on microstructure and electrical properties of thin films. A strong effect of chelating ligand was observed on nucleation, growth and microstructure of the film. PLZT thin film prepared with formamide as stabilizing agent showed improved dielectric and ferroelectric properties. A good correlation between microstructure and electrical properties has been established. Presence of dominant (100) lattice plane compared to (111) plane and improved grain growth has been considered as the key parameter for high ferroelectric and piezoelectric property in formamide based PLZTA thin films.

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