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Sol–gel preparation and characterization of calcium modified lead titanate (PCT) thin films

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Abstract

Thin ferroelectric films of calcium modified lead titanate $Pb_{1-x}Ca_xTiO_3$ where $x = 0.28$ (72:28) (PCT) are prepared by sol–gel spin coating process on ITO coated corning glass 7059 substrates. Sol–gel technology offers attractive features such as low processing temperature and ease of tailoring of the structural and electrical properties by controlling the composition of the films. Films are prepared using lead acetate trihydrate, calcium acetate hydrate and titanium isopropoxide as precursors, along with 2-methoxy ethanol as solvent and acetic acid as catalyst. Characterization of these films by X-ray diffraction show that the films exhibit tetragonal structure with perovskite phase. Replacement of calcium at Pb site in lead titanate results in reduction of tetragonal ratio (*c*/*a*), thus resulting in better electrical and ferroelectric properties. Atomic force microscope (AFM) images are characterized by slight surface roughness with a uniform crack free, densely packed structure. Dielectric, pyroelectric and ferroelectric studies carried out on these films have been reported and discussed. PCT shows fairly high voltage responsivity and appreciable detectivity. Moreover, its high value of remanent polarization (∼28 μC/cm^2) along with small value of coercive field (∼110 kV/cm) makes it a better suited material for non-volatile memory applications.

JEL classification: −77.55.+f

Keywords: A. Sol–gel processes; Lead calcium titanate; Pyroelectric sensor material

1. Introduction

Thin films of ferroelectric materials are being considered for applications in numerous electronic and electro-optic devices, e.g. non-volatile memories, optical waveguide devices, switching capacitors for integrated circuitry and pyroelectric devices [1,2]. The exploitation of ferroelectric thin films for electronic and electro-mechanical applications has been restricted due to limitations in deposition processes for device quality ferroelectric thin films. However, recent advances in thin film deposition technology, especially in the area of sol–gel technology have generated excitement within the ceramics community. The sol–gel method offers various advantages such as excellent control of stoichiometry, better homogeneity, film uniformity and ease of tailoring the properties by compositional variations. Lead titanate is known to have good piezo, pyro and ferroelectric properties. However, it has poor mechanical properties due to its large tetragonal ratio. Hence, several modifications of this material have been studied with the aim of obtaining improved electrical and mechanical properties to make them potentially useful for various applications. Calcium modified lead titanate with general formula $Pb_{1-x}Ca_xTiO_3$ (PCT) has received some attention because the substitution of Ca^{2+} for Pb^{2+} reduces the *c*/*a* ratio of the parent $PbTiO_3$ (PT) unit cell thereby resulting in better mechanical stability and enhanced properties [3–5]. In the present study, attempts have been made to prepare PCT ($x = 0.28$) thin films by sol–gel technique and their structural, electrical and pyroelectric properties have been investigated and presented in this paper.

2. Experimental

Films of chemical composition $Pb_{0.72}Ca_{0.28}TiO_3$ (PCT72/28) are prepared using lead acetate trihydrate, cal-

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cium acetate hydrate and titanium isopropoxide (all from Aldrich, USA) as precursors, along with 2-methoxy ethanol as solvent and acetic acid as catalyst. The sol is prepared by dissolving lead acetate trihydrate in acetic acid. 10 mol% lead acetate in excess of the stoichiometric ratio is added in order to compensate for lead loss during subsequent thermal treatment. The solution is refluxed at 110 °C for 3 h in a three-neck flask assembly to remove the water of crystallization. Similarly, calcium acetate hydrate is also dissolved in acetic acid and refluxed. Both the solutions are mixed together and refluxed with 2-methoxy ethanol. Finally, Titanium-isopropoxide in stoichiometric ratio is added to the solution with constant stirring to prepare PCT sol. Filtered sol is dispensed using a 0.2-μm syringe filter and spin coated at a speed of 3000 rpm for 30 s on ITO coated 7059 Corning glass substrate to deposit multiple coatings. After each coating, the films are heat treated to 150 °C to remove the volatile organics. The final crystallization is performed at 650 °C for 2 h by rapid heat treatment. The crystallinity and phases of the sintered films are examined using X-ray diffraction (Rigaku, Cu Kα radiation, $\lambda = 1.5405$ Å). The microstructure of the films is characterized by atomic force microscope. The film thickness is measured using Taly step method. Aluminium electrodes are vacuum deposited for dielectric and charge field hysteresis studies. Hysteresis studies are carried by Sawyer Tower circuit-RT66A. Dielectric properties of the films at various frequencies and temperatures are measured using an impedance analyzer. The pyroelectric current is measured after corona charging the films The pyro current is measured with a heating rate of 3 °C/min using Keithley electrometer model 610 C.

3. Results and discussion

The X-ray diffractogram of the PCT film is shown in Fig. 1. This diffractogram shows well resolved peaks. The lattice constants calculated using *h k l* values indicate that the "*c*" and "*a*" values for the unit cell are 3.97 and 3.89 Å, respectively. The *c*/*a* ratio of 1.02 suggests that the PCT72/28 film has perovskite structure with tetragonal phase. The fact that the film exhibits tetragonal phase with perovskite structure is also supported by the presence of well resolved (0 0 2) and (2 0 0) peaks in the diffractogram. In pure PT, the *c*/*a* ratio is about 1.06 [6]. The substitution of Ca in place of Pb reduces *c*/*a* ratio which may be explained on the basis of Ca ions occupying Pb ion sites with smaller ionic radius ($Ca^{2+} = 0.99$ Å, $Pb^{2+} = 1.20$ Å) resulting in shrinkage of the lattice. Microstructure of PCT films is studied by taking AFM images (3D and 2D) shown in Fig. 2. AFM images are characterized by slight surface roughness with a uniform crack free, densely packed microstructure. The surface roughness (RMS) of the films, calculated using the equipment's software routine, is 2.3 nm. The average grain size is found to be ∼100 nm.

The dielectric relaxation behaviour of the film is studied both as a function of frequency and temperature. The variations of dielectric constant ε_r and loss tangent $\tan\delta$ with frequency are shown in Fig. 3. Decrease in dielectric constant is observed with increase in frequency. The fall in dielectric constant arises from the fact that polarization does not occur instantaneously with the application of the electric field because of inertia. The delay in response towards the impressed alternating electric field leads to loss and decline

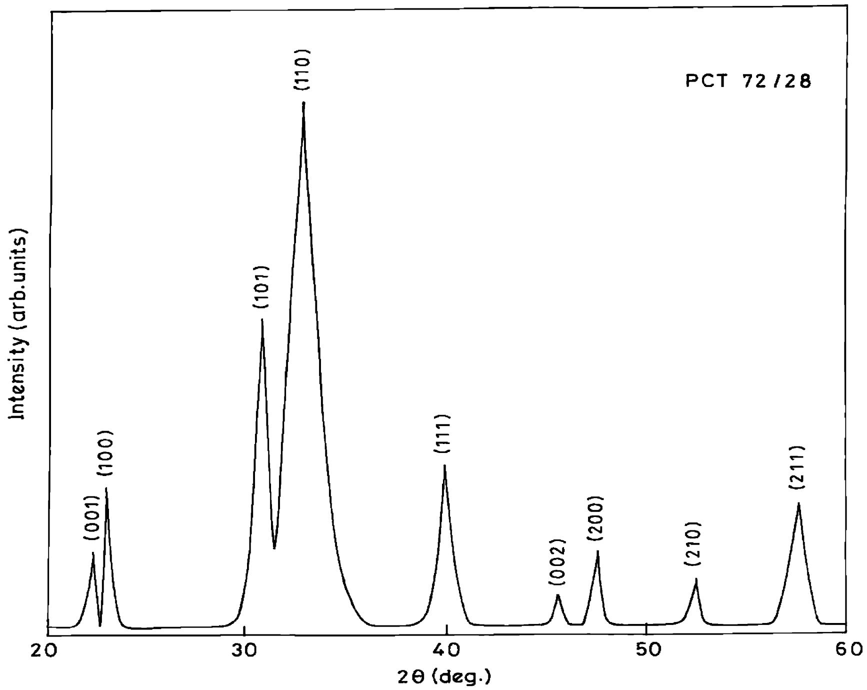

Fig. 1. X-ray diffractogram of PCT 72/28 film.

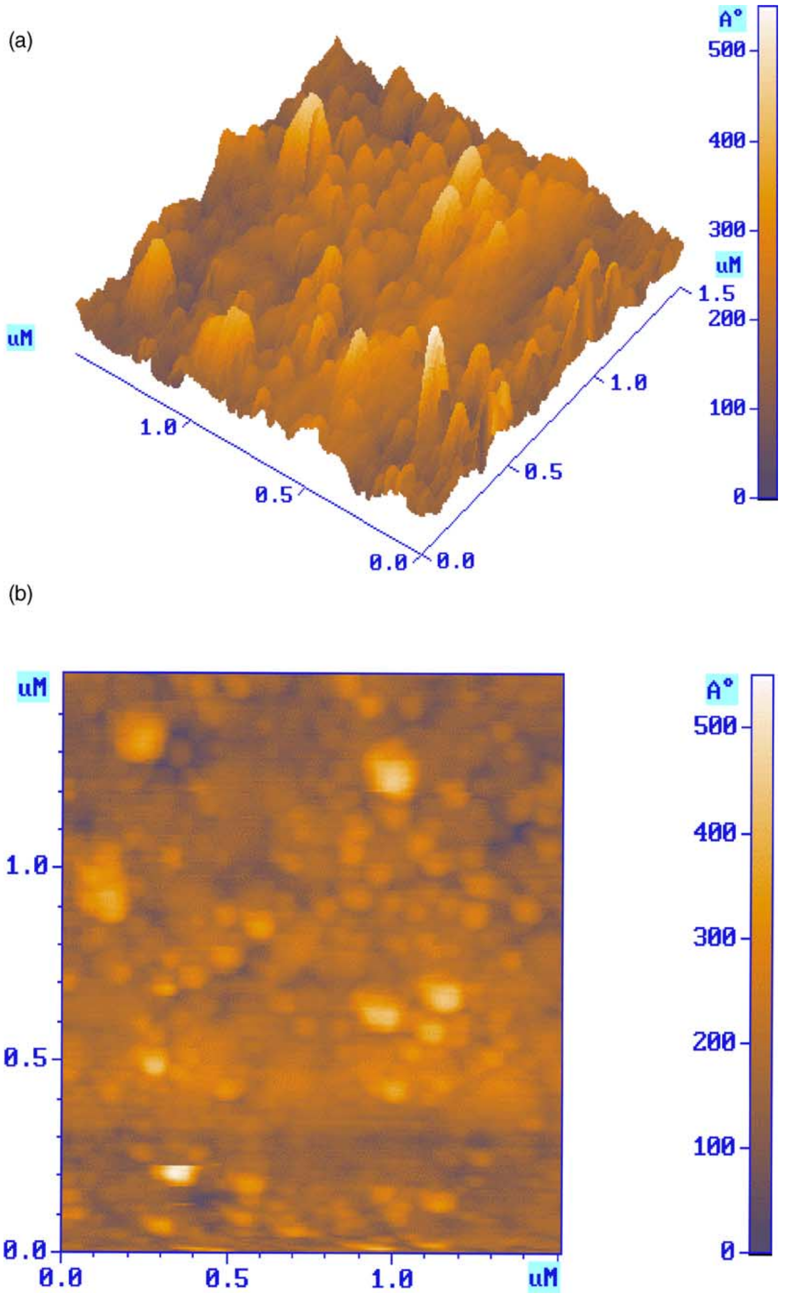

Fig. 2. (a) AFM (3D) image of PCT 72/28 film; (b) AFM (2D) image of PCT 72/28 film.

in dielectric constant. At low frequencies, all the polarizations contribute. As frequency is increased, those with large relaxation times cease to respond and hence the decrease in dielectric constant. The dielectric behaviour is typical of ferroelectric materials [7,8].

The observed variation of dielectric constant (ε_r) with temperature is shown in Fig. 4. The room temperature dielectric constant of PCT72/28 film is ~90 which is less than that reported for PT films ~115 [9]. There is a decrease in dielectric constant with addition of calcium in lead titanate. As reported earlier, addition of calcium has led to a decrease in c/a ratio. Thus, there is a decrease in dipolar response, thereby resulting in a decrease in dielectric constant at room temperature [10]. A peak is observed around 120 °C and is attributed to ferroelectric to paraelectric transition. This is much less than the transition temperature of PT(~490 °C) and is in agreement with the results reported by others [5]. The dielectric peaks are fairly broad as commonly observed in ferroelectric ceramic thin film and can be attributed to the compositional fluctuations and structural disorders. Most of the diffuse phase transitions studied in oxide ferroelectrics have occurred at temperature (<400 °C) where the disorders are likely to be frozen [11].

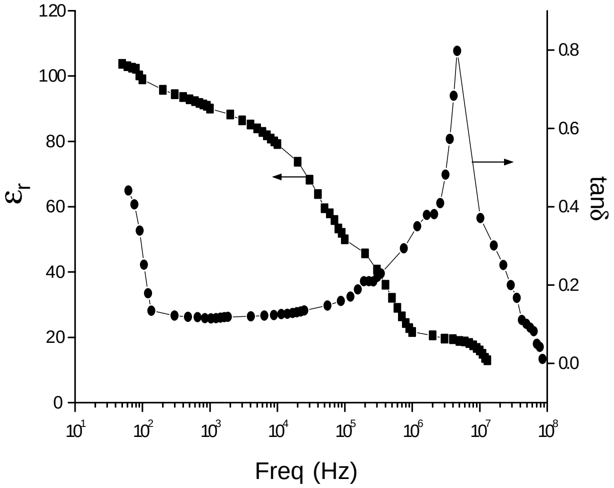

Fig. 3. Variation of ε_r and $\tan\delta$ with frequency of PCT72/28 film.

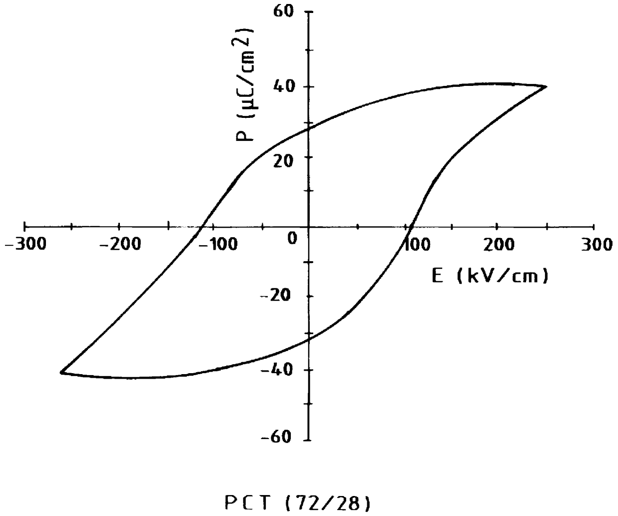

Fig. 5. Polarization–electric field hysteresis loop of PCT72/28 film.

The variation of pyrocoefficient P_i with temperature is also included in Fig. 4. It can be seen that pyrocoefficient increases with the increasing temperature in the ferroelectric region. The pyrocoefficient at room temperature is found to be about 46 nC/cm^2 K. The pyrocoefficient reported for lead titanate (bulk) is 40 nC/cm^2 K [12] and that for PT films is 15 nC/cm^2 K [5]. Thus, addition of calcium has resulted in an increase in pyrocoefficient significantly. Lead calcium titanate is both pyroelectric and piezoelectric [3,4] and the strain resulting from the thermal expansion results in the development of surface charges, thereby increasing P_i. As reported by Kholkin et al. [13], calcium addition increases the piezoelectric parameters and development of more surface charges takes place. This increases the pyroelectric current and the pyrocoefficient. Also, the variation of $P_i$with temperature is very small till 60 °C and hence is suitable for pyroelectric detectors. Pyroelectric figures of merit such as voltage responsivity $F_v = P_i/C_v\epsilon'$, current responsivity $F_i = P_i/C_v$ and detectivity $F_d = P_i/C_v(\epsilon'\tan\delta)^{1/2}$ have been calculated to evaluate the utility of the film for pyroelectric detectors. Here C_v is the specific heat of the ceramic at constant volume and is taken as 2.5 J/cm^3 K and $\epsilon' = \epsilon_0\epsilon_r$. These values at room temperature are found to be 18.4×10^{-11} A m/W, 2309 V cm^2/J and 1.89×10^{-5} Pa$^{-1/2}$, respectively. These values are higher than those reported for PT (films) and PCT (bulk) [5,14].

The polarization–electric field (*P*–*E*) hysteresis of PCT72/28 thin film measured at 60 Hz is shown in Fig. 5. The loop clearly confirms the ferroelectric nature of the film with a saturation polarization ∼40 μC/cm^2. The remnant polarization (P_r) and coercive field (E_c) are found to

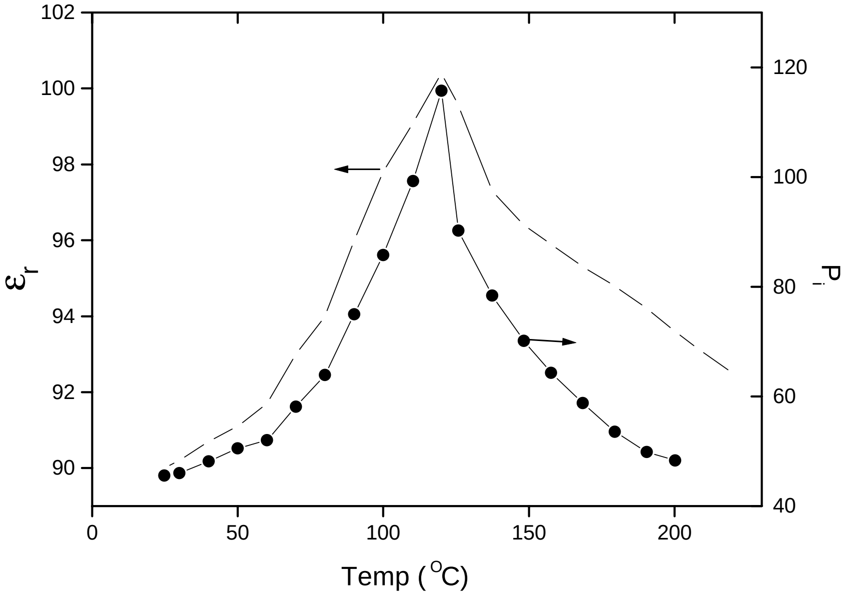

Fig. 4. Variation of ε_r and P_i with temperature at 1 kHz.

be ∼28 μC/cm^2 and ∼110 kV/cm, respectively. The difference between P_s and P_r (∼12 μC/cm^2) may be due to the result of a significant amount of free domain reversal after the removal of electric field. This could be attributed to domain walls having lower free energies at their original positions since they are stabilized by space charges or point defects. The values of spontaneous polarization and remanent polarization for PCT(72/28) are found to be more, in comparison with the values obtained by Tsuzuki et al. [15]. The remanent polarization (P_r) and coercive field (E_c) for PT films are reported to be ∼17 μC/cm^2 and ∼133 kV/cm, respectively [9]. Thus, the addition of calcium ion has increased the remanent polarization and decreased the coercive field. Generally, the ferroelectric properties strongly depend on grain size effect and internal stress effect. Water and solvent loss, organic decomposition and pyrolysis of nonvolatile species occurring during heating result in constrained shrinkage and residual tensile stress in the films [16]. Additionally, thermal mismatch effects between the substrate—film and phase transformations can also alter the residual stress state. It has been found from literature [17] that grain size decreases with increase in calcium doping. Theoretically, because of decrease in grain size, domain wall motion will be impeded leading to decrease in dipolar response. In our results, however remanent polarization increases with calcium ion doping. This may be due to the dominance of internal stress effect over the grain size effect. This internal stress results in a strong internal field which favors the ferroelectric state. Thus, the addition of calcium ion has increased the remanent polarization and decreased the coercive field, making it a better suitable material for memory applications.

4. Conclusion

It can be concluded on the basis of this study that PCT(72/28) films prepared by sol–gel technique exhibit tetragonal phase with perovskite structure. PCT(72/28) shows fairly high voltage responsivity and appreciable detectivity. The material also shows high value of P_r and low value of E_c. This shows that thin film of PCT(72/28) is a potential candidate for being used in pyrodetectors as well as memory devices.

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