



Ca Substituted PbTiO_3 Thin Films for Infrared Detectors

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Abstract. Crack free Ca substituted PT thin films have been deposited on ITO coated 7059 glass substrates by sol gel technique and crystallized at 650°C. Characterization of these films by X-ray diffraction show that the films exhibit tetragonal structure with perovskite phase. AFM, hysteresis, dielectric relaxation and pyroelectric studies have been carried out. The pyroelectric figures of merit of the films have been calculated. Our investigations show that these films are expected to give high infrared detector performance due to its high pyroelectric coefficient ($\sim 43 \text{ nC/cm}^2\text{K}$), high voltage responsivity ($\sim 2340 \text{ Vcm}^2/\text{J}$) and detectivity ($\sim 3 \times 10^{-5} \text{ Pa}^{-1/2}$) along with small value of dielectric constant (~ 83) and loss tangent (~ 0.04).

Keywords: sol gel technique, dielectrics, hysteresis, pyroelectric detector

Introduction

Ferroelectric thin films are being intensively investigated since they offer promising ferroelectric properties that are useful for various applications [1]. For many applications, PZT films are considered good candidates because of their high piezoelectric coefficients [2]. However, to increase the voltage response, Ti-rich compositions that offer low dielectric constants are desired. Pure PbTiO_3 (PT) with $T_c \sim 490^\circ\text{C}$ has large tetragonal distortion ($c/a = 1.06$) that prevents sufficient poling due to the large deformation associated with a 90° domain orientation. Hence, several modifications of this material have been studied for obtaining improved electrical properties to make them potentially useful for various applications [3, 4]. Calcium modified lead titanate has received attention because the substitution of Ca^{2+} for Pb^{2+} reduces the c/a ratio of the PT unit cell thereby resulting in better ferroelectric properties [4]. In the present studies, attempts have been made to prepare $\text{Pb}_{0.76}\text{Ca}_{0.24}\text{TiO}_3$ (PCT) thin films by sol gel technique and to investigate their structural, electrical and pyroelectric properties. This composition of PCT

has been selected due to the fact that it possess high electromechanical anisotropy, resulting in high pyroelectric effect [5].

Experimental Technique

Films of chemical composition $\text{Pb}_{0.76}\text{Ca}_{0.24}\text{TiO}_3$ (PCT) were prepared using lead acetate trihydrate, calcium acetate hydrate and titanium isopropoxide as precursors by the method described elsewhere [6, 7]. The crystallinity of the films was examined using X-ray diffraction (XRD). The surface morphology was studied by AFM pictures. The Fourier Transform Infrared (FTIR) spectra were examined by FTIR spectrophotometer. Aluminum top electrodes of 1 mm in diameter have been deposited in vacuum by electron beam evaporation unit (M/s Balzers, Leichtenstein, Switzerland) through a mask to form the ferroelectric capacitors for electrical measurements. Dielectric properties at various temperatures have been measured using an impedance analyzer (HP 4192 A). The P-E hysteresis loop measurements have been conducted using a Sawyer Tower circuit RT 66A (Radiant Technologies Inc.). The pyrocurrent has been measured

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after corona charging the films at 150°C for 30 minutes followed by cooling to room temperature in 20 minutes while the sample is still under the corona field. The corona voltage and current used are 7 kV and 50 μ A respectively. The pyrocurrent has been measured at a heating rate of 3°C/min using Keithley electrometer model 610°C. The pyroelectric current has been measured bidirectionally (on heating and cooling) and the mean value is taken; so as to eliminate the error due to the release of trapped charges.

Results and Discussions

The XRD of the PCT film (Fig. 1) shows well resolved peaks. The lattice constants calculated indicate that the “*c*” and “*a*” values for the unit cell are 4.02 Å and 3.86 Å. The *c/a* ratio of 1.04 suggests that the 76:24 PCT film has tetragonal phase. The fact that the film exhibits tetragonal phase with perovskite structure is also supported by the presence of well resolved (002) and (200) peaks in the diffractogram. In pure PT, the *c/a* ratio is about 1.06 [8]. This suggests that substitution of Ca in place of Pb reduces *c/a* ratio. This result may be explained on the basis of Ca ions occupying Pb ion sites with smaller ionic radius ($\text{Ca}^{2+} = 0.99\text{Å}$, $\text{Pb}^{2+} = 1.20\text{Å}$). The surface morphology was investigated by AFM and a 3D micrograph of the film is shown in Fig. 2. AFM is characterized by slight surface roughness with a uniform crack free microstructure. The surface roughness obtained from AFM software routine was found to be 3.65 nm which is lower than that obtained by Martin et al. [9] for films produced by laser ablation technique.

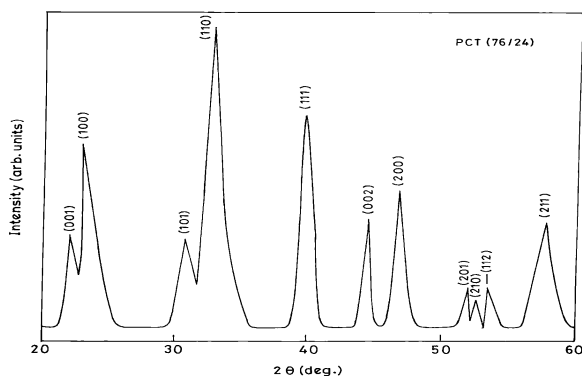


Fig. 1. X-ray diffractogram of PCT film.

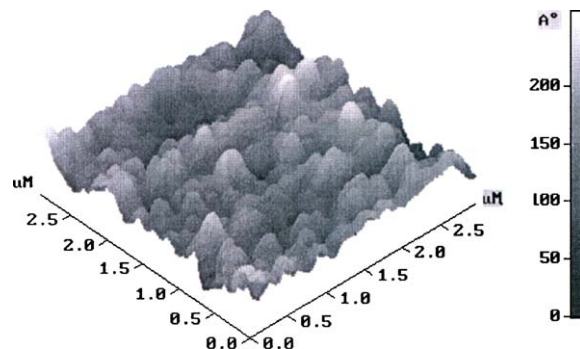


Fig. 2. AFM(3D) micrograph of PCT film.

Figure 3 shows the FTIR spectra of the as deposited and annealed (at 650°C) films on silicon substrates. The broad band around 3350 cm^{-1} corresponds to the (O–H) stretching vibration of hydroxyl groups of alcohols and water. The peaks present around 1410 and 1560 cm^{-1} can be ascribed to ν_{sym} ($-\text{COO}^-$) and ν_{asym} (COO^-) of acetyl groups respectively. The peaks around 1110 cm^{-1} may have contribution from two factors: due to the Ti–O–C vibration of propoxy groups directly bonded to titanium and due to the presence of native oxide prior to deposition. The small peaks around 1050 and 1010 cm^{-1} are the C–H rocking modes whereas, the peak around 950 cm^{-1} band belongs to the (C=C) + (C=O) stretching vibration modes of the organic group. The peak at 740 cm^{-1} is from the substrate and peak at 650 cm^{-1} is attributed to the M–O bonds, which come from the

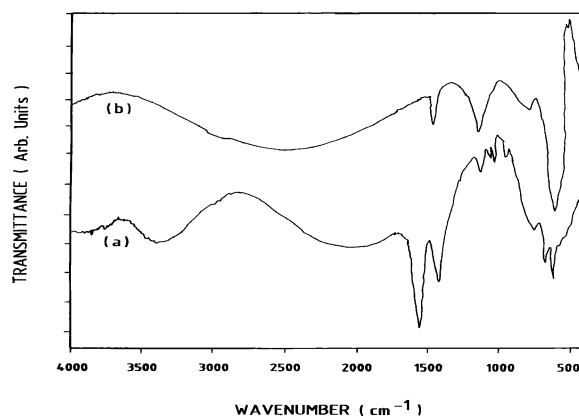


Fig. 3. FTIR Spectra of the PCT film (a) as deposited and (b) annealed at 650°C.

envelope of the photon bands of a metal-oxygen-metal bond of a solid network. The peak around 600 cm⁻¹ is from substrate occurring due to the Si-Si stretching mode. After annealing the film at 650°C, the broad band around 3350 cm⁻¹ and C-H rocking modes at 1050 and 1010 cm⁻¹ disappear completely while the intensity of the peak at 1410 cm⁻¹ decrease drastically. The peaks at 600, 740 and 1100 cm⁻¹ are due to the substrate. This suggests that PCT crystallizes at an annealing temperature 650°C. These results are qualitatively similar to those of Bao et al. [10].

The dielectric behaviour has been studied as a function of frequency. Decrease in dielectric constant (ϵ_r) is observed with increase in frequency as commonly observed in many ferroelectric ceramics [11].

Variations of ϵ_r and pyrocoefficient P_i with temperature at 50 Hz are shown in Fig. 4. The dielectric constant of PCT film is 83 which is less than that reported for PT films ~115 [12]. There is a decrease in ϵ_r with calcium. 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 ϵ_r [13]. A peak is observed around 135°C which is attributed to ferroelectric to paraelectric transition and is much less than the transition temperature of PT (490°C). Thus, addition of calcium ion has resulted in decrease of T_c and this is in agreement with others [14]. The dielectric peak is fairly broad as commonly observed in the ceramics and the broadening can mainly be attributed to the compositional fluctuations and structural disorders.

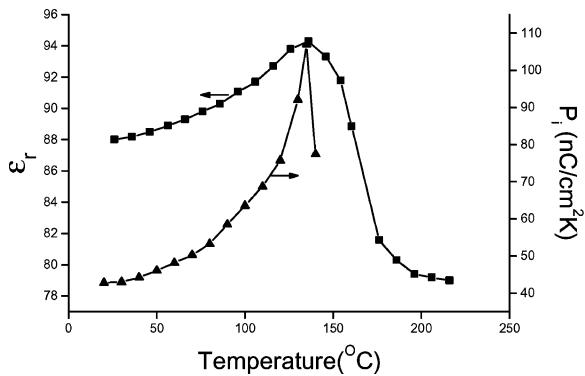


Fig. 4. ϵ_r and P_i vs. temperature of PCT film at 50 Hz.

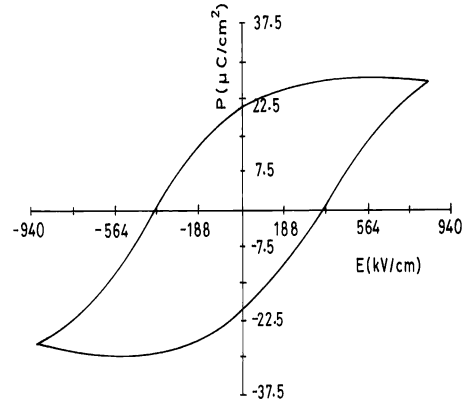


Fig. 5. P-E hysteresis loop of PCT film.

The polarisation-electric field curve of the film measured at 60 Hz is shown in Fig. 5. The loop clearly confirms the ferroelectric nature of the film with a saturation polarization $\sim 26 \mu\text{C}/\text{cm}^2$. The remanent polarization and coercive field are found to be $22 \mu\text{C}/\text{cm}^2$ and $369 \text{ kV}/\text{cm}$ respectively.

The P_i has been calculated using the relation $P_i = (I/A) (dT/dt)^{-1}$, where I is the pyroelectric current, A is the electrode area and dT/dt is the heating rate. The variation of P_i with temperature is shown in Fig. 4. It can be seen that P_i increases with increasing temperature in the ferroelectric region. The P_i at room temperature is $46 \text{ nC}/\text{cm}^2 \text{ K}$ while for PT, bulk and film form, it is $40 \text{ nC}/\text{cm}^2 \text{ K}$ [15] and $15 \text{ nC}/\text{cm}^2 \text{ K}$ [14] respectively. Thus, addition of calcium has resulted in an increase in P_i . Lead calcium titanate is both pyroelectric and piezoelectric [4, 5] and the strain resulting from the thermal expansion will result in the development of surface charges, thereby increasing P_i . As reported by Kholkin et al. [16], calcium addition increases the piezoelectric parameters and development of more surface charges takes place. This increases the pyroelectric current and thus P_i . 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 $F_d = P_i/C_v (\epsilon' \tan \delta)^{1/2}$ were calculated to evaluate the utility of the film for pyroelectric detectors. Here $C_v = 2.5 \text{ J}/\text{cm}^3 \text{ K}$ [15] and $\epsilon' = \epsilon_o \epsilon_r$. The observed values of ϵ_r , P_i and figure of merit of PCT film (76/24) are shown in Table 1, along with those reported for other pyroelectric materials [15, 17]. It can be seen that PCT(76/24) shows high F_v and appreciable F_d . Thus, it may be inferred that PCT (76/24) may be a better material for pyroelectric sensor device.

Table 1. Pyroelectric figures of merit of various pyroelectric materials at 50 Hz.

Properties	PCT 76/24 film	PCT bulk	PT film	PT bulk
ϵ_r	88	200	115	290
P_i (nC/cm ² K)	43	30	15	40
F_v (Vcm ² /J)	2208	700	589	600
F_i (10 ⁻¹¹ Am/W)	17.2	12	6	15.7
F_d (10 ⁻⁵ Pa ^{-1/2})	1.15	0.90	1.21	5.80

Conclusion

PCT (76/24) films are expected to give high infrared detector performance due to its high value of voltage responsivity and detectivity.

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