DIELECTRIC AND PYROELECTRIC STUDIES OF LEAD CALCIUM TITANATE THIN FILMS

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Abstract: Thin ferroelectric films of calcium modified lead titanate (Pbl,Ca,Ti03) have been prepared by sol gel spin coating process on ITO coated corning glass 7059 substrates. The values of x in our study are 0.20, 0.24 and 0.28. Characterization of these films by x-ray diffraction shows that the films exhibit tetragonal phase with perovskite structure. Dielectric, pyroelectric and ferroelectric studies carried out on these films have been reported and discussed. Dielectric constant of these films at room temperature varies from 78 to 90 while pyroelectric coefficient varies from 33 to 46 nC/cm2K. High pyroelectric figure of merit of PCT films have potential applications as pyroelectric sensor materials.

INTRODUCTION

A considerable amount of research has been focused on the growth and device fabrication of ferroelectric thin films for applications in piezoelectric transducers, pyroelectric infrared detectors and non-volatile random access memory devices [1]. Lead titanate (PT) has a large spontaneous polarization and a relatively small dielectric constant, which allow potentially important applications in the field of electronics and opto-electronics. However, this material has poor mechanical properties due to its large tetragonal strain. Hence, much attention has been focused on the modification of PT by doping, with the purpose of obtaining improved mechanical and electrical properties. If the Pb ion is replaced with an ion which has the same valency and smaller size, such as a Ca ion, this replacement will introduce a shrinkage of the lattice in the c-axis direction of the tetragonal phase and thus, the properties of PT are known to be varied by the addition of calcium[2]. The sol gel technique has been used with great success in producing high quality thin films[3-5]. Calcium modified lead titanate films (PCT) have received some attention, due to its decreased tetragonality and better pyroelectric and piezoelectric properties [6]. In this paper, the structural, pyroelectric and ferroelectric properties of Pb., Ca, Ti03 (PCT) films (with x=0.20,0.24 and 0.28) prepared by sol gel method have been discussed.

SOL GEL FILMS PREPARATION AND CHARACTERIZATION

PCT films of chemical composition Pb,80 Ca0.20 Ti03 (PCT80/20), Pb0.76 Ca0.24 Ti03 (PCT 76/24) and Pb0.72 Ca0.28 Ti03, (PCT72/28) have been prepared by sol gel technique[4-5]. The thickness of the films is determined using Taly-step method. The film structures are characterized with X-ray diffractometer (Rigaku miniflex, Japan, CUK, radiation, h=1.5405 A).

RESULTS AND DISCUSSIONS

The observed XRD patterns presented in "Fig. 1" show well resolved peaks. The lattice constants (c and a) of the unit cell calculated by using hkl values for PCT films (with x=0.20,0.24 and 0.28) are 4.03, 4.02, 3.97 and 3.89 respectively. The XRD study shows...
that 'c' value decreases while value of 'a' increases with calcium concentration. The same results have also been found by others [7]. These results may be explained on the basis of Ca ions occupying Pb ion sites with smaller ionic radius (Ca\(^{2+}\) = 0.99\(\text{Å}\), Pb\(^{2+}\) = 1.20\(\text{Å}\)). The c/a ratio of all the compositions (x=0.20, 0.24 and 0.28) are 1.05, 1.04 and 1.02 and suggest that the films have perovskite phase with tetragonal structure. The tetragonality decreases with increase of the Ca content.

Room temperature (RT) variation of dielectric constant and loss tangent with frequency are shown in "Fig.2" and "Fig.3". The observed values of room temperature dielectric constant (E\(_r\)) and loss tangent (tan\(\delta\)) of PCT films measured respectively at 100Hz are given in Table I. 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 as charges have inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant. The same type of frequency dependent dielectric behaviour is found in many ferroelectric ceramics [8]. The initial decrease of tan 6 with increasing frequency may be described on the basis of Koops phenomenological model [9]. Subsequently, tan 6 increases with further rise in frequency and shows maximum in the 1-10 MHz region because the active component (ohmic) of the current increases more rapidly than its reactive component (capacitive). At higher frequencies (>2MHz), tan 6 decreases with increasing frequency because the active component of the current is practically independent of frequency and the reactive component increases in proportion to the frequency. This type of variation has been observed in some of the dielectrics [10].

The observed variations of dielectric constant with temperature for all the compositions are shown in "Fig.4". The increase in dielectric...
constant with calcium addition is due to the decrease of tetragonality and ease of 90° domain orientation. Dielectric peaks observed indicate that the Curie temperature $T_c$ of PCT 80/120, PCT 76/24 and PCT 72/28 is about 190°C, 135°C and 120°C respectively. It turns out that $T_c$ decreases with increase in calcium doping and this is in agreement with the results reported by others[11]. The dielectric peaks are fairly broad as commonly observed in ferroelectric ceramics in thin films form and the broadening can mainly attributed to the compositional fluctuations and structural disorders.

In all the films, ferroelectric polarization vs electric field loops have been observed and are shown in "Fig. 5". The remanent polarization ($P_r$) increases with increase in Ca content while the coercive field ($E_c$) first increases for $x=0.24$ and then decreases for $x=0.28$. Generally the $P_r$ and $E_c$ values observed in thin films are known to depend strongly on the grain size and internal stress[11]. It has been found from literature survey [13] that grain size decreases with increase in calcium doping. 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. Additionally, thermal mismatch effects between the substrate and the film and phase transformations can also alter the residual stress state. The combined effect of grain size and internal stress may lead to increase in coercive field in PCT(76/24). However, decrease in coercive field in PCT(72/28) might be because of the internal stress effect becoming more pronounced as compared to that due to grain size effect. 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. [14].

The pyroelectric coefficient ($P_i$) is calculated using the relation $P_i=I/A \left(\frac{dT}{dt}\right)$, where $I$ is the pyroelectric current measured during the third heating cycle when it shows reproducible values, $A$ is the electrode area and $\frac{dT}{dt}$ is the heating rate. The variation of $P_i$ with temperature is shown in "Fig. 5". The pyrocoefficient increases with temperature for all the compositions. Lead calcium titanate is both pyroelectric and piezoelectric [2,15] and the strain resulting from the thermal expansion will result in the development of surface charges, thereby increasing $P_i$. As reported earlier[6], calcium addition increases the piezoelectric parameters and development of more surface charges takes place. This increases the pyroelectric current and thus, the pyrocoefficient. The corresponding Curie temperatures of the peak values of $P_i$ are nearly equal to those determined in the dielectric studies of the materials. The observed values of pyroelectric coefficient $P_i$ of PCT films are given in Table 1.

![Graph of dielectric constant vs temperature](image1.png)

**Fig.4** Variation of dielectric constant with temperature of PCT films

![Graph of polarization vs electric field](image2.png)

**Fig.5** Polarization-Electric field hysteresis loop of PCT films
The efficiency or figure of merit of a pyroelectric sensor is evaluated in several ways; for example, voltage responsivity \( F_v = Pe/C_C \), current responsivity \( F_i = Pi/C_i \), and detectivity \( F_d = Pi/Cv(\Delta t) \). Here \( C_C \) is the specific heat of the ceramic at constant volume and is taken as 2.5 J/cm\(^3\)K and \( E' = \Delta \varepsilon \). The figures of merit have been calculated at 100Hz because most of the pyroelectric devices operate at low frequencies (usually 100Hz). The calculated values of \( F_v \), \( F_i \) and \( F_d \) at 100Hz of PCT films are also compared in Table I. It can be seen that PCT(76/24) shows fairly high voltage responsivity and appreciable detectivity. Thus it may be inferred that PCT (76/24) may be utilized for pyroelectric sensor device.

**CONCLUSION**

The structural and electrical properties of sol-gel derived films have been studied. The pyrocoefficient and figures of merit have been calculated and it is observed that PCT films show quite good pyroelectric properties. PCT (76/24) is expected to give high infrared detector performance due to its high value of voltage responsivity and detectivity along with smaller value of dielectric constant and loss tangent. Hence, the use of sol gel derived (Pb,Ca) TiO\(_3\) films is expected to enhance greatly the application of the material for pyroelectric infrared detectors.

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**REFERENCES**


**Table I: Various parameters of PCT thin films**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Composition</th>
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<tbody>
<tr>
<td>( E )</td>
<td>PCT (80/20)</td>
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<tr>
<td>( E' )</td>
<td>83</td>
</tr>
<tr>
<td>( \tan )</td>
<td>0.0755</td>
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<tr>
<td>( P_i (nC/cm^2K) )</td>
<td>33</td>
</tr>
<tr>
<td>( F_i (10^7 Am/W) )</td>
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<tr>
<td>( F_v (V/cm^2J) )</td>
<td>1796</td>
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<tr>
<td>( F_d (10^5 Pa^{-1/2}) )</td>
<td>1.77</td>
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<td>( P_l (pC/cm^2) )</td>
<td>3.70</td>
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<tr>
<td>( p (pC/cm^2) )</td>
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<tr>
<td>( E_k (kV/cm) )</td>
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