# The Effect of Mn Doping on the Dielectric Properties of Lead Strontium Titanate (PST)

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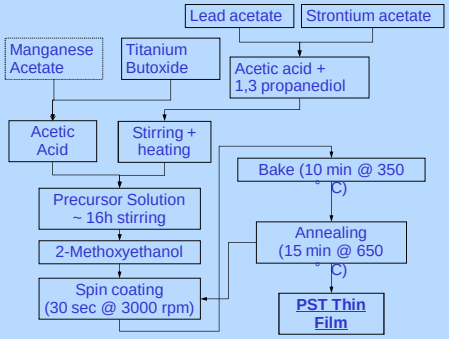
## Abstract

A modified sol-gel method was used to fabricate $(Pb_{0.4}Sr_{0.6})(Mn_xTi_{1-x})O_3$ (Mn doped PST) thin films with x = 0, 0.01, 0.03, and 0.05 on Pt/Ti coated $SiO_2$/Si substrates. The structure, surface morphologies, dielectric and tunable properties of these films were investigated as a function of Mn content (x). X-ray diffraction, scanning electron microscopy and atomic force microscopy analysis showed that all the films were well crystallised with random orientation. It was found that the grain size/roughness, dielectric constant, loss, tunability and figure of merit (FOM) are affected by the Mn doping level. Further on it was found that the ferroelectricity increases with Mn content. The dielectric constant reached a maximum of 1100 and the maximum figure of merit (FOM) was 23.96 with 3 mol% Mn; whereas the maximum value of the tunability was 76.72% at 10 V with 1 mol% Mn.


## Film Preparation




## Mathematical Model

### Tunability

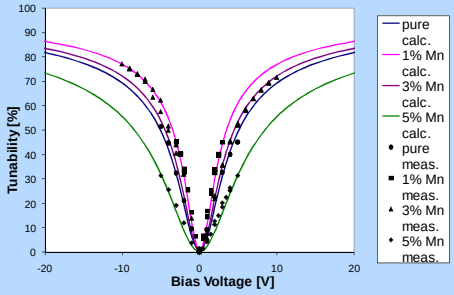
The Theory of the non-linear Response of Ferroelectrics – non-zero bias field

$$n = \frac{C_{max}}{C_{min}} \quad \text{or} \quad n(\%) = \frac{C_{max} - C_{min}}{C_{max}} \cdot 100$$

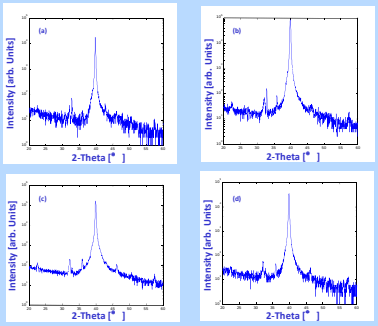
It can be shown that the voltage dependent Capacitance can be expressed as:

$$C(V) = \frac{C_{max}}{\cosh\left[\frac{2}{3}\sinh^{-1}\left(\frac{2V}{V_2}\right)\right] - 1}.$$

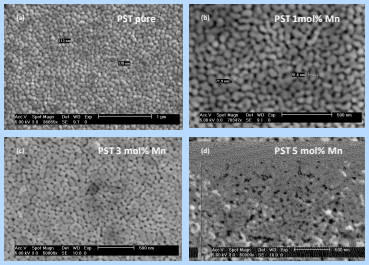
Where $V_2$ is the applied Voltage where $C(V)=C_{max}/2$ .



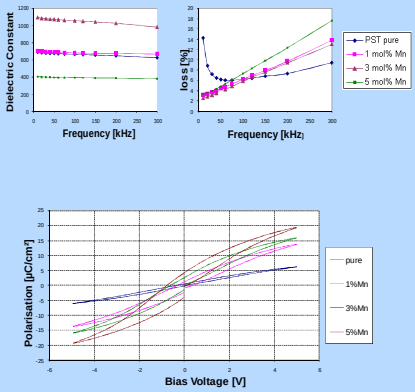

## XRD Measurements



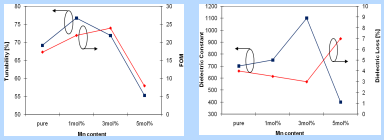

## SEM Imagines




## Properties at Zero Bias




## Comparison



## Comparison

**The Reason for the Increase of the Dielectric Constant for x < 0.03**

1. Oxygen vacancies are generated by heat treatment under non-oxidising atmosphere

$$2Ti^{4+} \rightarrow 2Ti^{3+} + V_O^{\bullet\bullet}$$

2. Mn is a "freakish", multivalence ion – it can appear as $Mn^{2+}$, $Mn^{3+}$ and $Mn^{4+}$

$$\frac{1}{2}O_2 + Mn^{2+} + V_O^{\bullet\bullet} \rightarrow Mn^{4+} + O_O^x \qquad \frac{1}{4}O_2 + Mn^{2+} + \frac{1}{2}V_O^{\bullet\bullet} \rightarrow Mn^{3+} + \frac{1}{2}O_O^x$$

$$\Rightarrow \begin{cases} 2Ti^{4+} + Mn^{2+} + \frac{1}{2}O_2 \leftrightarrow 2Ti^{3+} + Mn^{4+} + O_O^x \\ 2Ti^{4+} + Mn^{2+} + \frac{1}{4}O_2 \leftrightarrow 2Ti^{3+} + Mn^{3+} + \frac{1}{2}O_O^x \end{cases}$$

In other words: **$Mn^{2+}$ doping consumes oxygen vacancies in PST**

x < 0.02: $Mn^{2+}$ doping consumes oxygen vacancies, thus providing a larger polarisation path. **The dielectric constant increases**

x ~ 0.02: The positive charge of the oxygen vacancies is totally balanced by the negative of $Mn^{2+}$, $Mn^{3+}$, or $Mn^{4+}$. **The system is saturated.**

Max Tunability ~80% with 2% loss → FOM = 40

x > 0.02: **Electron hopping between $Mn^{2+}$, $Mn^{3+}$ and $Mn^{4+}$ begins**. The hopping conduction due to the hopping of the charge carriers between Mn sites begins to occur in 2 mol% Mn doped PST, and then becomes distinct in 5 mol% doped films. **This lowers in the end the dielectric constant and increases the loss in PST thin films**

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