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FABRICATION AND CHARACTERIZATION OF STRONTIUM DOPED CALCIUM TITANATE THIN FILMS

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Abstract

Strontium doped calcium titanate, $Ca_{1-x}Sr_xTiO_3$ (x = 0.1, 0.2, 0.3, 0.4) thin films deposited onto silicon substrates were prepared by sol-gel method and heated at 700°C for 1 hr. The sol-gel method offers numerous advantages such as good homogeneity of the powders and low processing temperature. Microstructural observation of the $Ca_{1-x}Sr_xTiO_3$ thin films was investigated from scanning electron microscopy (SEM) images and it was found that the grain sizes varied with increase in concentration of strontium. The structural identification with different dopant concentrations of the films examined using X-ray diffraction (XRD) analysis showed the complete crystallization in the perovskite structure. Capacitance-voltage (C-V) measurements were carried out by using a LCR meter for various frequencies (0.1 kHz to 100 kHz) and the values of dielectric constant for all the films were also determined.

Keywords: $Ca_{1-x}Sr_xTiO_3$ thin films, SEM, XRD, C-V

Introduction

$CaTiO_3$ belong to the perovskite class materials (ABO_3) and it is also a chemistry and thermally stable ceramic oxide, which is widely studied due to its dielectric and photoluminescent properties. $CaTiO_3$(CTO) has an orthorhombic structure and it has a dielectric permittivity of approximately 180 at room temperature that changes with experimental conditions [Malic, B. et al., (2007)]. Perovskite materials have been extensively studied due to a wide range of low-temperature structural distortions. These structures have become fundamental interests in physics in technological applications such as microwave devices and phase transitions. The $CaTiO_3$ based solid solution can also be applied as high performance capacitors. They usually undergo several phase transitions with increase in temperature and pressure [Mascot, M., Fasquelle, D. and Carru, J. C. (2011)].

$CaTiO_3$ is one of the most important ferroelectric perovskite which has been considerably used for radioactive waste and as a dopant in electric materials due to its dielectric behaviors and flexibility in structural transformations. Four phases of CTO were suggested by using neutron diffraction method at ambient pressure. As temperature decreases, CTO undergoes a sequence of phase transitions [Jae-Yeol Hwang et al., (2006)]. Body centered tetragonal (T > 1580 K) cubic (T = 1580 K), centered orthorhombic (T = 1500 K) and primitive orthorhombic (T = 1380 K). Unfortunately phase transition temperature has not yet pinpointed experimentally the possible number of phases of CTO. However, the high-pressure behavior of CTO at room temperature is not clear. CTO has the ideal cubic perovskite structure for temperature at 1580 K. In which the structure have been demonstrated the stability under high temperature and pressure. An investigation on cubic CTO is carried out because of its suggested analogy with geologically

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relevant ABO_3 perovskites under high pressure and temperature. Therefore pressure analogy can be developed with temperature due to direct correspondence [B.D. Lee, H.R. .et.al., (2005)]. First principles calculations of $CaTiO_3$ were also performed by Cockayne et al. and Wang et al., but they were mainly focused on the dielectric constant, optical properties, and the surface structures. Like higher temperatures, when the pressure is relatively large enough by bond compression, than up to what extent material show stable phase. Theoretically, phase transitions between different structure phases under temperature and pressure are difficult to characterize [T. Bongkran and W. Khiawwangthong, (2008)].

Various methods can be performed to synthesize $CaTiO_3$, including sol-gel, precipitation, mechano-chemical milling, electro-chemical deoxidation, mechanical alloying and hydrothermal. Each of these methods has advantages and disadvantages. Sol-gel is a promising method for the preparation process is simple, in addition to the product produced has crystallinity better than the other method [F. M. Pontes et al., (2000)]. In this study, strontium doped calcium titanate thin films were synthesized by sol-gel method to improve the good crystallinity of the product.

Experimental Details

Strontium doped calcium titanate, $Ca_{1-x}Sr_xTiO_3$ (x = 0.1, 0.2, 0.3, 0.4) powders were synthesized by solid state reaction method, using high purity (99.9 % reagent grade) CaO, SrO and TiO_2 powders. These powders were weighed on the basis of stoichiometric composition. The resultant, stoichiometric compositions of powders were ground by agate mortar to obtain the homogeneity. Each mixed powder was annealed at 700°C for 1 hour and mixed with 2-methoxyethanol ($CH_3OCH_2CH_2OH$) solution and then heated up to 100˚C with indirect heat treatment for 1 hr. Finally, homogeneous precursor solutions were obtained. The silicon substrates are cleaned by standard cleaning method. The resulting precursor solutions are deposited on silicon substrates by spin coating technique. After spin coating, deposited thin films are heat treated at 700˚C for 1hr. The surface morphology and the thickness of the films were analyzed by scanning electron microscope (SEM). X-ray Diffraction analysis was used as the major tool for identification of phase of prepared thin films. The capacitance- voltage measurements and the dielectric properties of the films were carried by using LCR meter.

Results and Discussion

Morphological Analysis

The surface morphology and the cross sectional view of the strontium doped calcium titanate thin films were evaluated using scanning electron microscopy as shown in Fig 1 (a-h). SEM images indicated that all the films were composed of densely packed microcrystals. The values of the average grain sizes and thickness of the thin films were presented in Table 1. The average grain size increases with the increasing of strontium content.

Table 1 The values of the average grain sizes and thickness of the strontium doped calcium titanate thin films

Thin film	Average Grain Size (μm)	Thickness (μm)
10% Sr doped $CaTiO_3$	0.45	7.8
20% Sr doped $CaTiO_3$	0.48	8.8
30% Sr doped $CaTiO_3$	0.58	10.7
40% Sr doped $CaTiO_3$	0.59	11.4

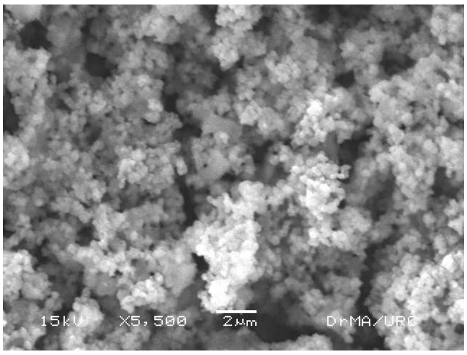

Figure 1 (a) SEM image of 10% Sr doped CTO thin film

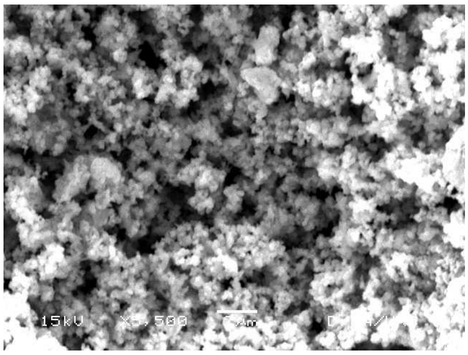

Figure 1 ((b) SEM image of 20% Sr doped CTO thin film

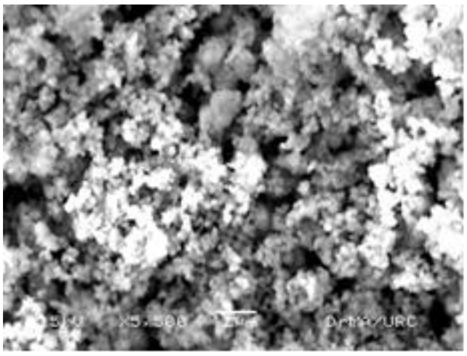

Figure 1 (c) SEM image of 30% Sr doped CTO thin film

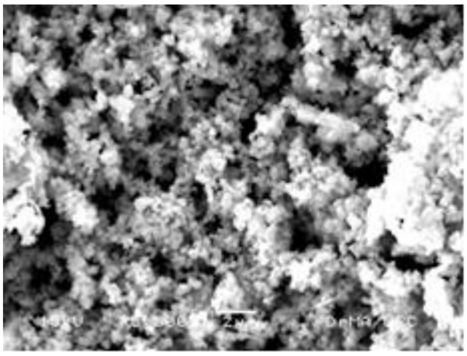

Figure 1 (d) SEM image of 10% Sr doped CTO thin film

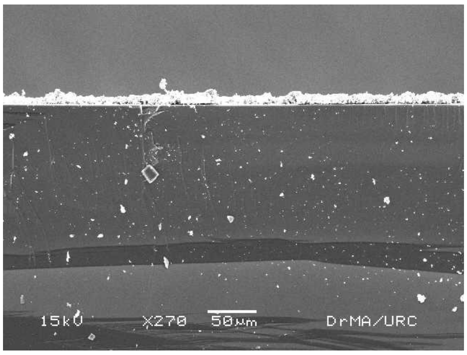

Figure 1 (e) Cross sectional image 10% Sr doped CTO thin film

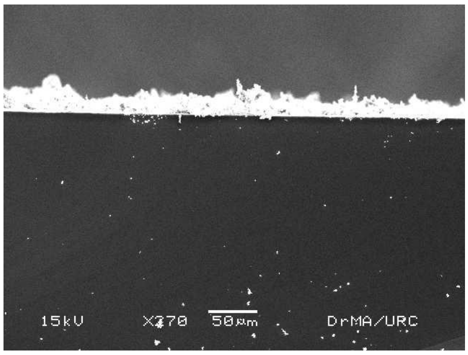

Figure 1 (f) Cross sectional image 20% Sr doped CTO thin film

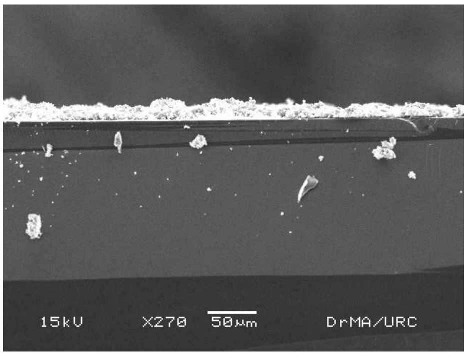

Figure 1 (g) Cross sectional image 30% Sr doped CTO thin film

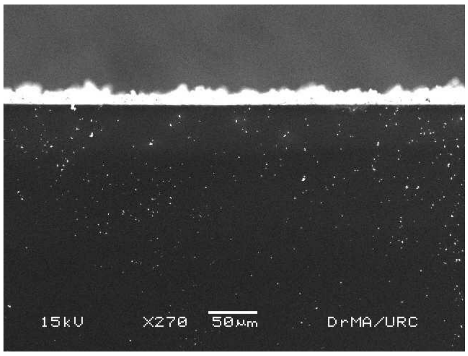

Figure 1 (h) Cross sectional image 40% Sr doped CTO thin film

Structural Analysis

XRD characterization was conducted to obtain the information both quantitatively and qualitatively on the crystal structure of $CaTiO_3$. Based on the diffraction pattern can be determined the crystal phases and crystallite sizes of $CaTiO_3$ samples. The samples were scanned from (2θ = 22.755 – 23.36) using XRD machine with Cu source which has a wavelength of 0.154 nm. X-ray diffraction pattern of strontium doped calcium titanate thin films onto silicon substrates with various dopant concentrations are shown in Fig 2 (a-d). The characteristics peaks in the XRD patterns confirmed the presence of CST material and also indicated that all the films are well crystallized and orthorhombic perovskite structure. The lattice parameters were slightly increased with the increasing of strontium content. The variation in the lattice parameters of strontium doped CTO thin films with change in dopant concentration may be attributed to the change in ionic radius. The XRD patterns showed that the increased dopant concentration leads to decrease in intensity of diffraction peaks with preferred orientation at (110) planes. The crystallite size was calculated using Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

The (hkl) plane, full width half maximum (FWHM) and crystallite sizes (D) of all the films are listed in Table 2 (a-d).

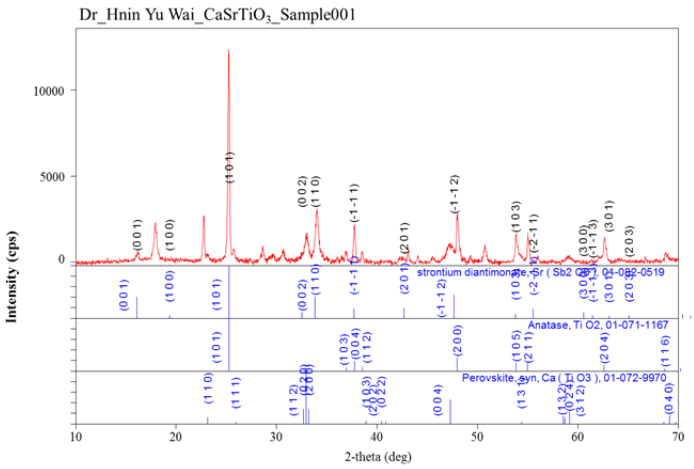

Figure 2 (a) X-ray diffraction of 10% Sr doped $CaTiO_3$ thin film

Table 2 (a) (hkl) plane, full width half maximum (FWHM) and crystallite sizes (D) of $Ca_{1-x}Sr_xTiO_3$ (x = 0.1) thin film

N0	(hkl) plane	FWHM (deg)	Crystallite size (nm)
1	(101)	0.19	40.747
2	(110)	0.48	16.207
3	(103)	0.12	62.778
Average crystallite size			39.911

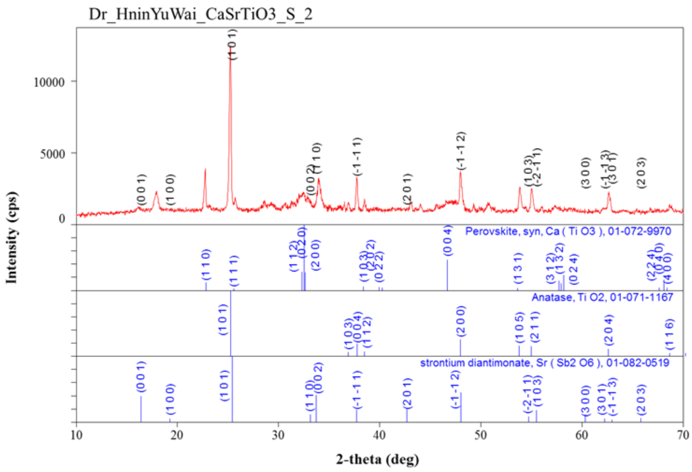

Figure 2 (b) X-ray diffraction of 20% Sr doped $CaTiO_3$ thin film

Table 2 (b) (hkl) plane, full width half maximum(FWHM) and crystallite sizes (D) of $Ca_{1-x}Sr_xTiO_3$ (x = 0.2) thin film

No	(hkl) plane	FWHM (deg)	Crystallite size (nm)
1	(101)	0.168	48.494
2	(110)	0.420	18.530
3	(103)	0.164	43.324
Average crystallite size			36.783

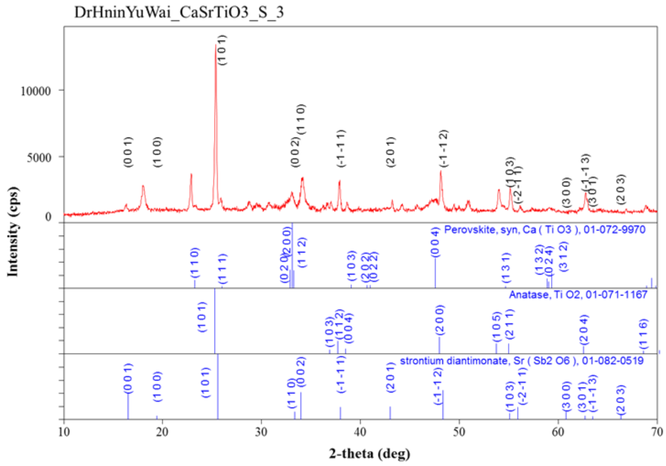

Figure 2 (c) X-ray diffraction of 30% Sr doped $CaTiO_3$ thin film

Table 2 (c) (hkl) plane, full width half maximum(FWHM) and crystallite sizes (D) of $Ca_{1-x}Sr_xTiO_3$ (x = 0.3) thin film

N0	(hkl) plane	FWHM (deg)	Crystallite size (nm)
1	(101)	0.197	39.340
2	(110)	0.179	43.499
3	(103)	0.090	83.307
Average crystallite size			55.382

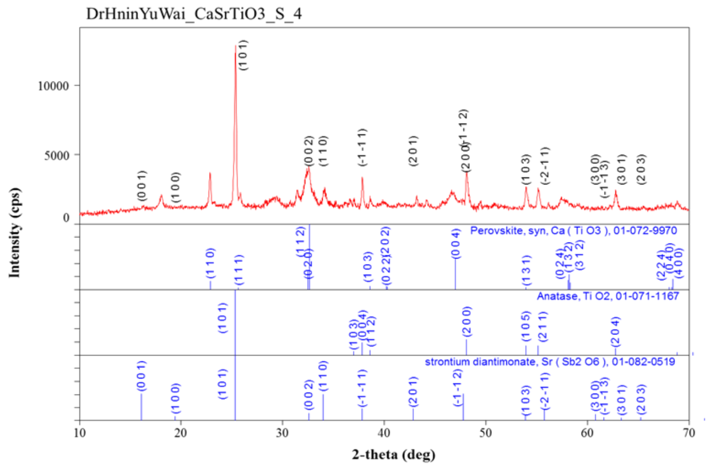

Figure 2 (d) X-ray diffraction of 40% Sr doped $CaTiO_3$ thin film

Table 2 (d) (hkl) plane, full width half maximum(FWHM) and crystallite sizes (D) of $Ca_{1-x}Sr_xTiO_3$ (x = 0.4) thin film

N0	(hkl) plane	FWHM (deg)	Crystallite size (nm)
1	101	0.184	43.312
2	110	0.174	44.759
3	103	0.130	57.956
Average crystallite size			48.675

Table 3 The peak positions(2θ), full width half maximum(FWHM), lattice parameters and crystallite sizes (D) of strontium doped calcium titanate thin films at (110) plane

Thin Films	(hkl) plane	Peak Positions (2θ)	FWHM	Lattice parameter	D (nm)
10% Sr doped $CaTiO_3$	(110)	23.36	0.48	a = 5.2783 b = 5.5408 c = 7.5520	16.207
20% Sr doped $CaTiO_3$	(110)	23.17	0.42	a = 5.3882 b = 5.4711 c = 7.6789	18.530
30% Sr doped $CaTiO_3$	(110)	22.861	0.179	a = 5.4871 b = 5.5053 c = 7.7251	43.499
40% Sr doped $CaTiO_3$	(110)	22.755	0.174	a = 5.4792 b = 5.5383 c = 7.7719	44.759

Dielectric Properties

The dielectric constants of strontium doped calcium titanate thin films were calculated from capacitance-voltage measurements at the frequency range of 0.1 kHz to 100 kHz. The dielectric constant varies with the applied voltage. The dielectric constant (ε) can be calculated by the equations below,

$$C_0 = \varepsilon_0 A/t,$$

$$\varepsilon = C/C_0$$

where

C = capacitance using the material as the dielectric in the capacitor,

C_0 = capacitance using vacuum as the dielectric

ε_0= Permittivity of free space (8.85 x 10^{-12} F/m)

A = Area of the plate/ sample cross section area

t = Thickness of the sample

The maximum value of dielectric constant was occurred at the 20% strontium doped calcium titanate thin film measured in a frequency range of 0.1 kHz. The dielectric constant of the films as function of frequency and strontium content are shown in Fig 3 (a & b) and the results are listed in Table 4.

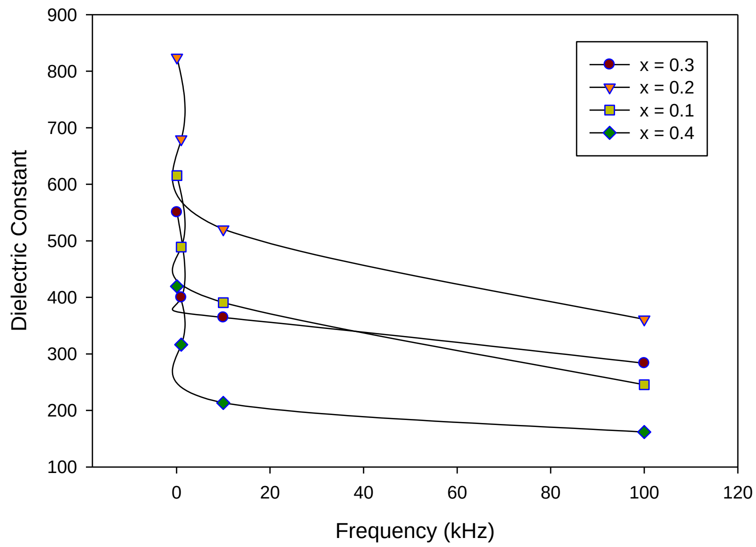

Figure 3 (a) The dependence of dielectric constant of the Sr doped $CaTiO_3$ thin films as a function of frequency

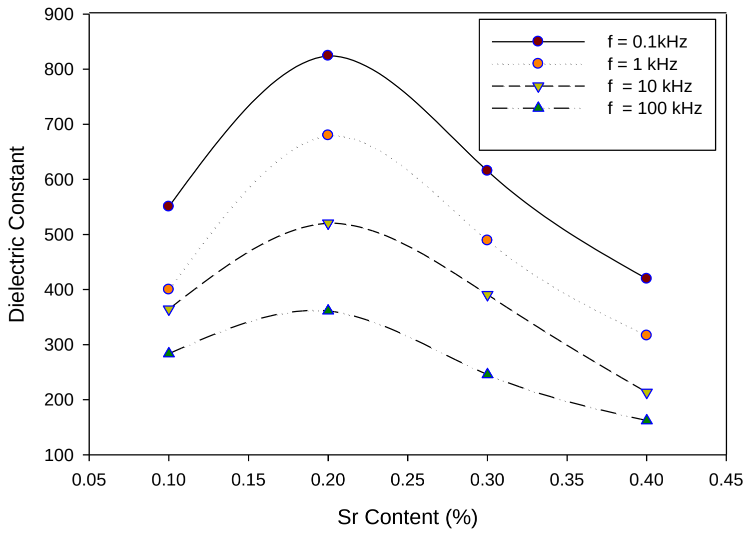

Figure 3 (b) The dependence of dielectric constant of the $CaTiO_3$ thin films on the Sr content

Table 4 The values dielectric constant of Sr doped $CaTiO_3$ thin films as a function of frequency

Thin Films	Dielectric Constant			
	f = 0.1 kHz	**f =1kHz**	**f = 10kHz**	**f = 100kHz**
10 % Sr doped $CaTiO_3$	550.3499616	399.6955028	364.3960678	283.535652
20 % Sr doped $CaTiO_3$	824.3014282	679.7182784	520.4414423	361.1646061
30 % Sr doped $CaTiO_3$	615.2501695	488.9084746	390.6911186	245.4707797
40 % Sr doped $CaTiO_3$	419.4169492	316.3661017	213.3152542	161.7898305

Conclusions

Strontium doped calcium titanate, $Ca_{1-x}Sr_xTiO_3$ (x = 0.1, 0.2, 0.3, 0.4) thin films deposited onto silicon substrates were prepared by sol-gel method. SEM images showed that all the films were composed of densely packed microcrystals. XRD patterns indicated that all the films were well crystallized and orthorhombic perovskite structure. The lattice parameters were slightly increased with the increasing of strontium content. Widening the diffraction pattern is influenced by the crystallite size, where the wider diffraction pattern indicates the smaller crystallite size. XRD patterns of strontium doped calcium titanate thin films were observed a better polycrystalline nature oriented along with (110) planes. The maximum value of dielectric constant was occurred at the 20% strontium doped calcium titanate thin film measured in a frequency range of 0.1 kHz. The dielectric constants of the films decrease with the increasing frequencies. These results suggested that strontium concentration offers a good control of structural and dielectric properties.

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