STRUCTURAL AND ELECTRICAL PROPERTIES OF Ba DOPED $CaTiO_3$ THIN FILMS

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Abstract

Calcium titanate and barium doped calcium titanate, $Ca_{1-x}Ba_xTiO_3$ (x = 0.1, 0.2, 0.3) thin films deposited onto silicon substrates were prepared by spin coating technique. The prepared undoped and Ba doped $CaTiO_3$ thin films were studied by various characterization techniques aimed at understanding the structural and electrical properties of the samples. These films were characterized by a smooth surface with uniform, crack-free microstructure and densely packed, which is in agreement with the scanning electron microscopy (SEM) analysis. The effect of composition on the phase formation of these samples was investigated by recording X-ray diffraction patterns (XRD) and it was observed that the lattice parameter varied with increasing the dopant concentration of barium. The dielectric constants of all the films were determined by a capacitance-voltage measurement using a LCR meter in the frequencies range of (0.1 kHz to 100 kHz).

Keywords : Calcium titanate thin films, SEM, XRD, Capacitance-voltage

Introduction

Calcium titanate ($CaTiO_3$) is one of a group of metal titanate compounds with a perovskite structure $CaTiO_3$ has long been known as a ceramic dielectric with a high dielectric constant and large positive temperature coefficient. Electroceramics based on $CaTiO_3$ has been studied various physical properties by a number of researchers [T. Bongkran and W. Khiawwangthong,(2008)]. Physical properties of $CaTiO_3$ that have been studied including electrical properties, especially electrical conductivity, while the optical properties were widely studied including the nature of the absorption of UV-Vis and photoluminescence performance.

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 [W. Sun, Y. et al., (2010)].

The $CaTiO_3$ based solid solution can also be applied as high performance capacitors. $CaTiO_3$ has an important application in microwave communication systems. $CaTiO_3$ also be used as an electronic ceramic material in particular as ferroelectric materials and dielectric materials in general. $CaTiO_3$ has an orthorhombic structure and it has a dielectric permittivity of approximately 180 at room temperature that changes with experimental conditions[E. Cockayne, B.P. Burton, (2000)].

They usually undergo several phase transitions with increase in temperature and pressure. It is utilized in the construction of field devices and sensors for the study of rheology of earth mantle and in the electroceramic industry [Xiaoyong Wei and Xi Yao,(2007)]. The dopants

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induce polarization giving rise to lattice distortion in this compound. So far only a handful amount of crystallographic data for $CaTiO_3$ with different dopants is available in the literature. Generally it is revealed that crystal structure of $CaTiO_3$ is orthorhombic which confirmed by X-ray diffraction experiments [P. Boutinaud, E. Tomasella, A. Ennajdaoui, R. Mahiou, (2006)].

In the present study, synthesis of pure $CaTiO_3$ as well as doped with Ba on B-Site has been carried out through conventional solid-state reaction method. The effect of Ba content on the structural, morphological and electrical properties of the $CaTiO_3$ thin films were studied.

Experimental Details

Calcium titanate, $CaTiO_3$ and barium doped calcium titanate, $Ca_{1-x}Ba_xTiO_3$ (x = 0.1, 0.2, 0.3) thin films were synthesized by solid state reaction method, using high purity CaO, BaO and TiO_2 powders. These powders were weight on the basis of stoichiometric composition. The resultant, stoichiometric composition of the mixed powders were ground by agate mortar to obtain the homogeneity and the mixed powders were annealed at 700°C for 1 hour. Each powder was mixed with 2-methoxyethanol ($CH_3OCH_2CH_2OH$) solution and then heated up to 100˚C with indirect heat treatment for 1hr. Finally, homogeneous precursor solutions or coating solutions were obtained. The silicon substrates were cleaned by standard cleaning method. The resulting precursor solutions were deposited on silicon substrates by spin coating technique. After spin coating, deposited thin films were heat treated at 700˚C for 1hr. The surface morphology and the thickness of the films were analyzed by scanning electron microscope (SEM). The phase and crystallinity of the films were characterized by X-ray diffraction (XRD) analysis with Cu-$K_{\propto 1}$ radiation. The capacitance- voltage measurements and the dielectric properties of the films were carried by using LCR meter.

Results and Discussion

SEM Analysis

The surface morphology and the cross sectional view of the undoped and barium doped calcium titanate thin films were evaluated using SEM as shown in Fig 1 (a-h). These results showed a well-developed grain size and dense microstructure in all samples. 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 barium content. The effect of doping on grain size is usually interpreted in terms of dopant solubility and distribution of doping ions between the surface and interior parts of the grain.

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

Thin films	Average Grain Size (μm)	Thickness (μm)
Undoped $CaTiO_3$	0.35	7.5
10% Ba doped $CaTiO_3$	0.41	9.4
20% Ba doped $CaTiO_3$	0.42	9.1
30% Ba doped $CaTiO_3$	0.48	5.9

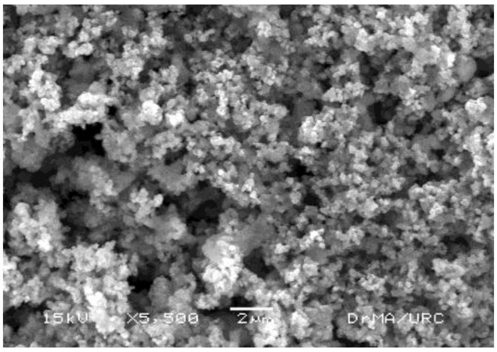

Figure 1 (a) SEM image of CT thin film

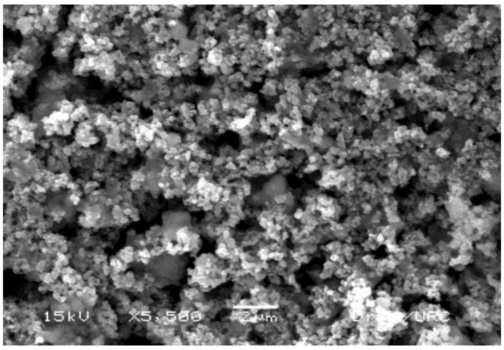

Figure 1 (b) SEM image of 10% Ba doped CT thin film

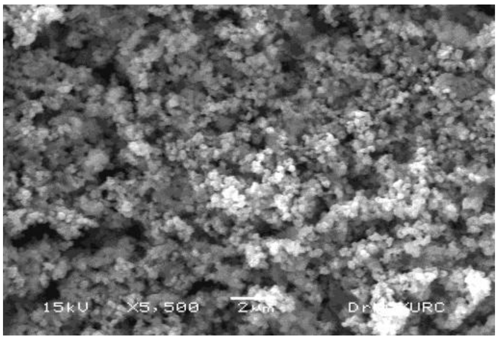

Figure 1(c) SEM image of 20% Ba doped CT thin film

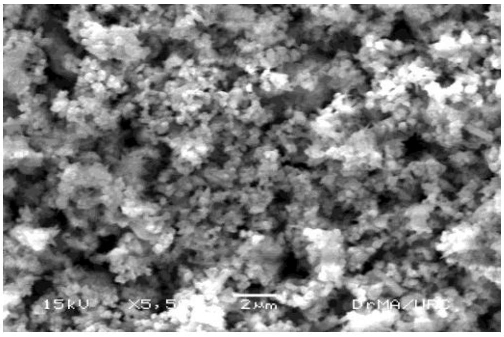

Figure 1 (d) SEM image of 30% Ba doped CT thin film

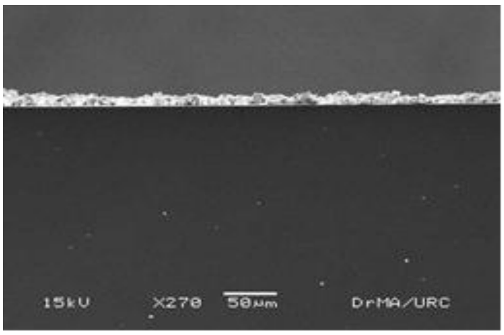

Figure 1 (e) Cross sectional image CT thin film

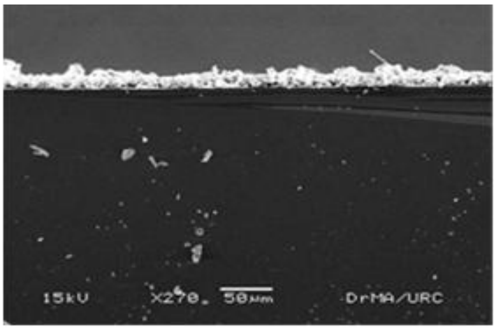

Figure 1 (f) Cross sectional image 10% Ba doped CT thin film

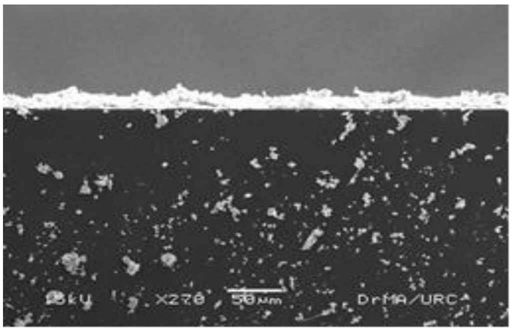

Figure 1 (g) Cross sectional image 20% Ba Ba doped CT thin film

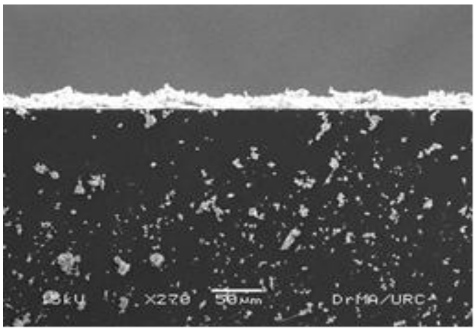

Figure 1 (h) Cross sectional image 30% doped CT thin film

X-ray Diffraction (XRD) Analysis

Structural properties of Ba doped $CaTiO_3$ samples were studied by X-ray diffraction from which can be determined the crystal phase and crystallite size of $CaTiO_3$ samples. Fig. 2(a-d) show the X-ray diffraction pattern for the $CaTiO_3$ samples with different dopant concentration of barium. There were significant differences in the diffraction patterns of each sample indicating that the dopant material affects the structural properties of the samples. 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 = 27.624 - 48.010) using XRD machine with Cu source which has a wavelength of 0.154 nm. Widening the diffraction pattern is influenced by the crystallite size, where the wider diffraction pattern indicates the smaller crystallite size. Average crystal size (ACS) can be calculated based on widening the diffraction peaks using Scherrer formula by the equation below

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

The peak position, full width half maximum (FWHM) and crystallite sizes (D) of $CaTiO_3$ and barium doped calcium titanate, $Ca_{1-x}Ba_xTiO_3$ (x = 0.1, 0.2, 0.3) thin films are listed in Table 2.

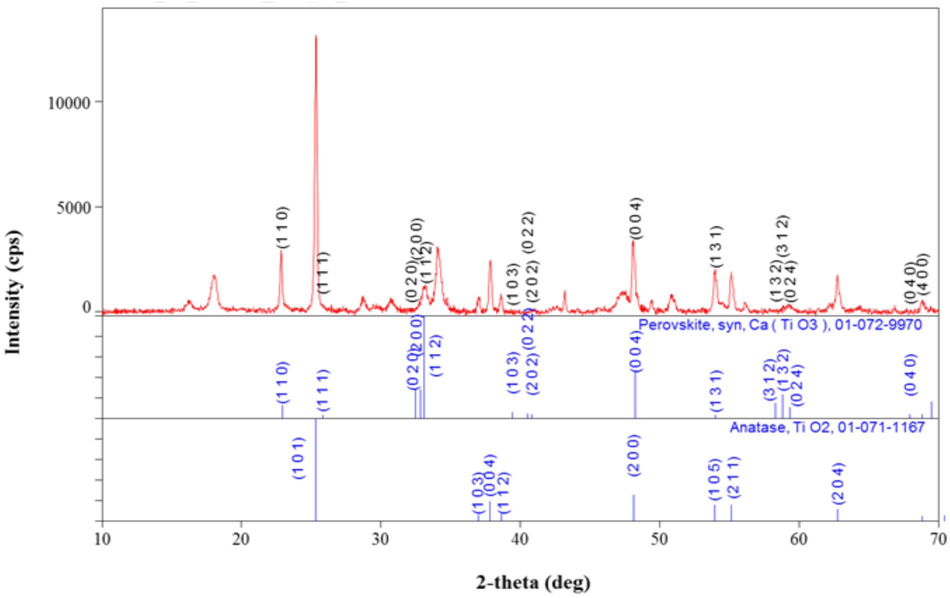

Figure 2 (a) X-ray diffraction of $CaTiO_3$ thin film

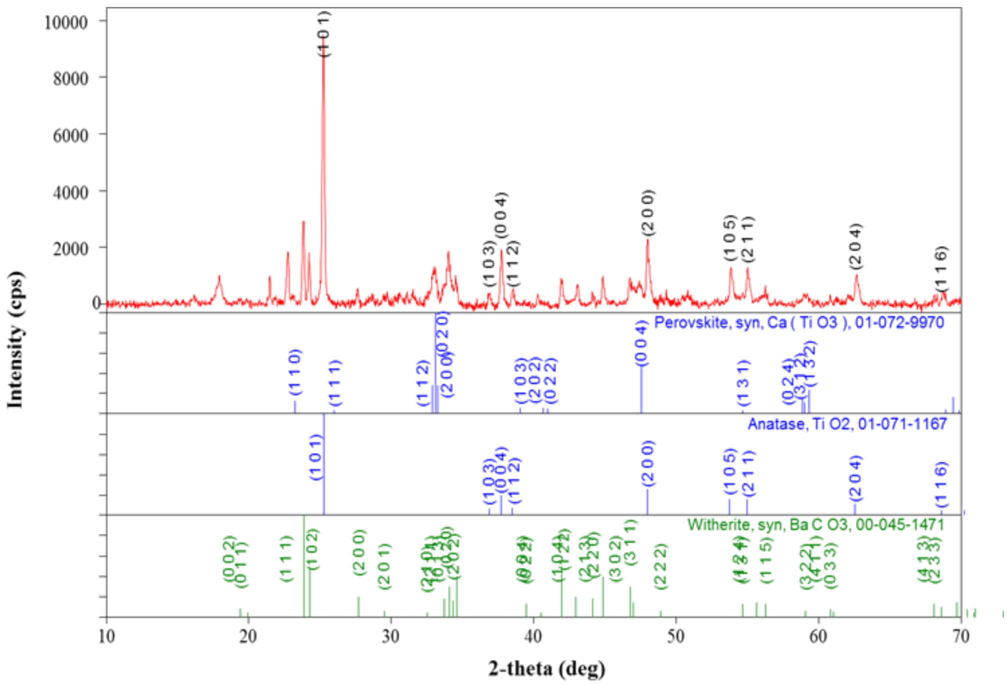

Figure 2 (b) X-ray diffraction of 10% Ba doped $CaTiO_3$ thin film

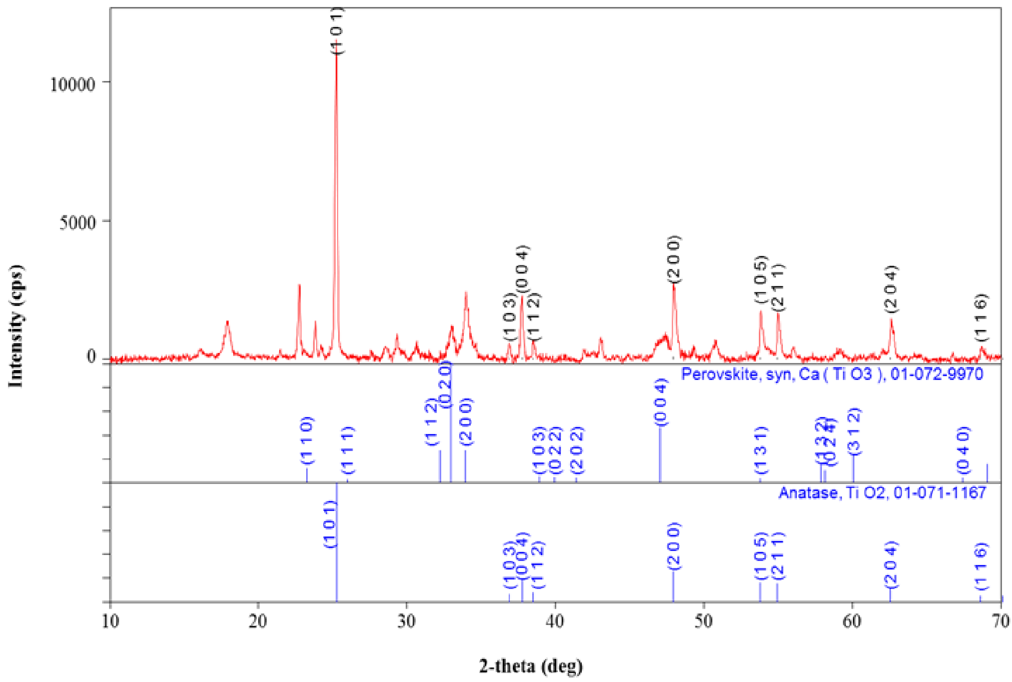

Figure 2 (c) X-ray diffraction of 20% Ba doped $CaTiO_3$ thin film

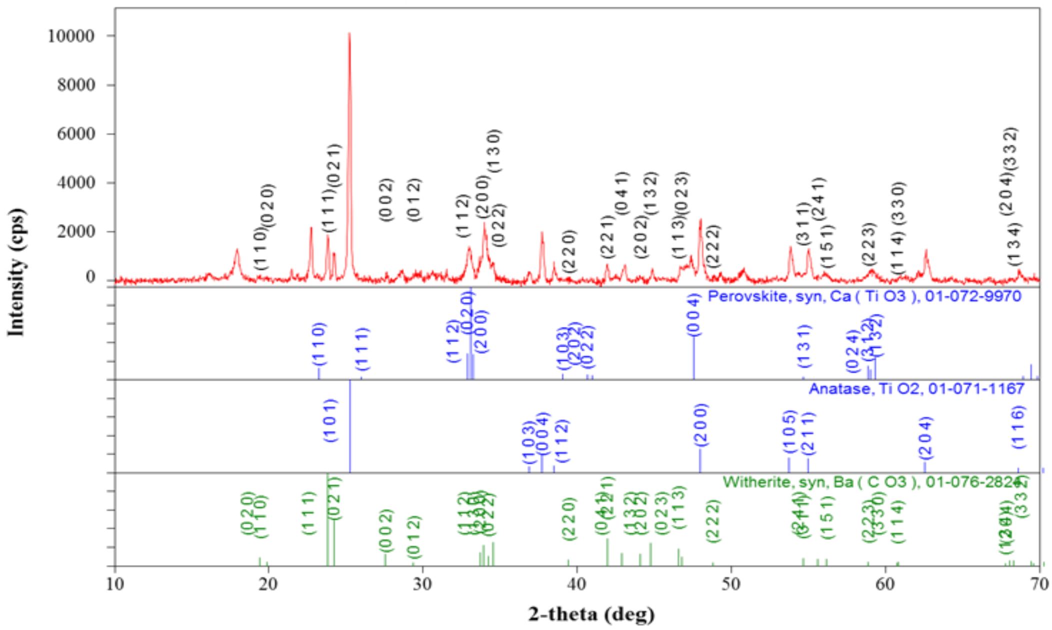

Figure 2 (d) X-ray diffraction of 30% Ba doped $CaTiO_3$ thin film

Table 2 The peak positions (2θ), full width half maximum (FWHM), lattice parameters and crystallite sizes (D) of undoped and Ba doped $CaTiO_3$ thin films at (200) plane

Thin Films	(hkl) plane	Peak positions (2 θ)	FWHM	Lattice parameter	D (nm)
Undoped $CaTiO_3$	(200)	33.111	0.48	a = 5.4501 b = 5.5129 c = 7.5388	17.267
10% Ba doped $CaTiO_3$	(200)	34.010	0.416	a = 5.2790 b = 5.5523 c = 7.7190	19.971
20% Ba doped $CaTiO_3$	(200)	48.010	0.145	a = 5.3850 b = 5.4965 c = 7.6692	59.999
30% Ba doped $CaTiO_3$	(200)	27.624	0.120	a = 5.3805 b = 5.4819 c = 7.6918	68.184

Dielectric Properties

The dielectric constants of undoped and barium doped calcium titanate, $Ca_{1-x}Ba_xTiO_3$ (x = 0.1, 0.2, 0.3) thin films were evaluated from capacitance-voltage measurements at the frequency range of 0.1 kHz to 100 kHz. 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 (8.85×10^{-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 10% barium doped calcium titanate thin film measured in a frequency range of 0.1 kHz. The frequency dependence of the dielectric constants for undoped and barium doped calcium titanate thin films are shown in Fig 3 (a & b) and the results are listed in Table 3.

Table 3 The values dielectric constant of undoped and Ba doped $CaTiO_3$ thin film as a function of frequency

Thin Films	Dielectric Constant			
	f = 0.1 kHz	f =1kHz	f = 10kHz	f = 100kHz
Undoped $CaTiO_3$ thin film	433.8983	271.7186	258.3050	111.7694
10% Ba doped $CaTiO_3$ thin film	735.8434	573.3333	310.1333	273.3333
20% Ba doped $CaTiO_3$ thin film	451.3189	407.3928	373.8757	105.36497
30% Ba doped $CaTiO_3$ thin film	430.3290	392.3163	347.3092	101.1065

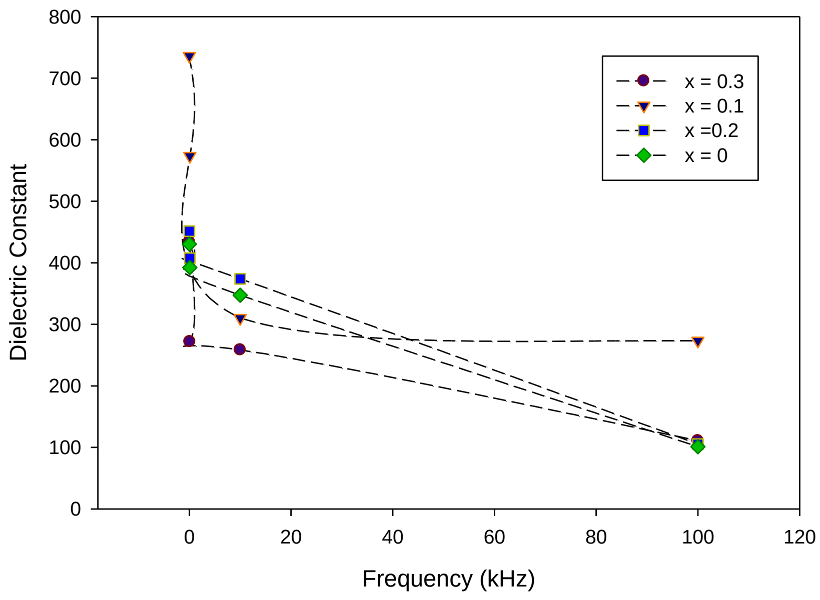

Figure 3 (a) The dependence of dielectric constant of the $CaTiO_3$ thin films as a function of frequency

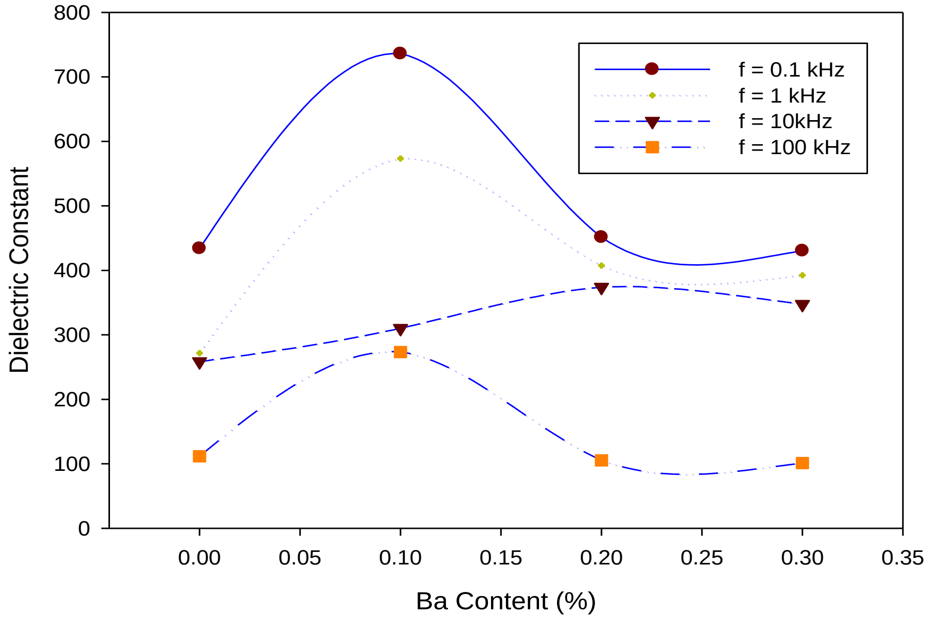

Figure 3 (b) The dependence of dielectric constant of the $CaTiO_3$ thin films on the Ba content

Conclusions

Calcium titanate, $CaTiO_3$ and barium doped calcium titanate, $Ca_{1-x}Ba_xTiO_3$ (x=0.1, 0.2, 0.3) thin films were successfully synthesized by the sol-gel method. SEM results showed the existence of well-developed grain sizes and dense microstructures in all samples. The average grain size increases with the increasing of barium content. XRD patterns indicated that all the films were well crystallized and orthorhombic perovskite structure. The lattice parameters were slightly increased with the increasing of barium content. The dielectric constants of all the films were determined by a capacitance-voltage measurement and the maximum value of dielectric constant was occurred at the 10% barium doped calcium titanate thin film measured in a frequency range of 0.1 kHz. These results showed that the morphological, structural and electrical properties of the films were dependent on the barium concentrations.

Acknowledgements

The authors sincerely thank Professor Dr Khin Khin Win, Head of Department of Physics, University of Yangon, for her kind permission to carry out this research.

I would like to express my sincere thanks to Dr Myo Lwin, Professor, Department of Physics, Dr Ye Chan, Professor and Head, Universities' Research Center, Dr Aye Aye Thant, Professor, Department of Physics, Dr Yin Maung Maung, Professor, Department of Physics and Dr Than Zaw Oo, Professor, Universities' Research Center, University of Yangon, for their permission to this paper.

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