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Der Pharma Chemica, 2014, 6(3):17-23
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Influence of ER doping on the microstructural and dielectric properties of microwave sintered calcium copper titanate

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ABSTRACT

The present work reports synthesis, as well as a detailed characterization of structural, morphological and dielectric properties of Er doped $CaCu_3Ti_{4-x}Er_xO_{12}$ (CCTEO) with x = 0.00, 0.02, 0.10, 0.20 and 0.50 mol% ceramics were prepared by sol-gel route. The prepared samples were sintered by using microwave sintering. The phase composition and microstructure were studied by means of X-ray diffraction (XRD) and high resolution scanning electron microscopy (HRSEM). The crystal structure did not change on doping with erbium; and it remained cubic when all the six compositions were studied. At lower frequencies, it was found that the dielectric constants had a maximum value at 0.5 mol% of Er. This result indicates that a certain amount of Er dopant can be improve the dielectric properties of $CaCu_3Ti_4O_{12}$.

Keywords: Ceramics; Sol-gel; Microwave sintering; Microstructure; Dielectric properties

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INTRODUCTION

The high dielectric constant that was reported for Centro symmetric perovskite related calcium copper titanate ($CaCu_3Ti_4O_{12}$) ceramics has drawn the attention of many researchers around the globe [1–11]. The crystal lattice structure of this ceramic is composed of titanate oxide crystals arranged in a cubic perovskite structure with Im3 space group and a lattice parameter of 7.391 A°. The TiO6 octahedron is tilted and, as a consequence, the coordination of Ca and Cu cations is altered, producing a square planar arrangement of the oxygen around the Cu^{2+} cations and a 12-coordinate icosahedral environment for Ca.2 [12].

Since an anomalously giant dielectric constant (ε_r) of $CaCu_3Ti_4O_{12}$ (CCTO) was first reported by Subramanian et al. [13]. Due to these unique dielectric properties, it is theorized that CCTO ceramics are a promising material for use in many electronic applications such as capacitors, memory devices, gas sensors, humidity sensors, varistors and microwave device applications [13-17] and it does not present phase transition [12].

It was demonstrated that the electrical properties of CCTO ceramics are strongly dependent upon their micro-structure [14, 18-20]. Several explanations for the origin of high dielectric constant for CCTO have been proposed mainly based on bulk property contributions as against the microstructural features which in turn are affected by the ceramic processing conditions including sintering temperatures as well as the ambience [4, 13, 21, 22].

If the high dielectric constant is due to intrinsic effects such as stoichiometric changes, oxygen vacancies, Cu segregation, and different oxidation states of Ti and Cu or due to extrinsic effects related to the microstructure, as stated by the Internal Barrier Layer Capacitance (IBLC) model [12]. It is now widely accepted that the giant dielectric response in CCTO ceramics is attributed to an extrinsic effect [23].

IBLC mechanism states that conducting grains and insulating grain boundaries give rise to high value of dielectric constant. It has been observed that dielectric and microstructural properties in CCTO are processing conditions dependent. Size of grain and thickness of grain boundaries generally depend on sintering duration [24]. To improve dielectric properties of CCTO ceramics, the influences of doping ions substituted into Ca^{2+}, Cu^{2+}, Ti^{4+}, and O^{2-} sites in CCTO crystal lattices have been extensively investigated [15, 16, 25-32].

Developing high dielectric materials synthesized with lower calcination/sintering temperature have become the subject of study for researchers. While some recently published reports concentrate on different synthesis techniques to reduce the processing temperature, other reports focus on substitutions to change the material property. However, very limited work on the effects of substituting impurity along with lower processing temperature CCTO was reported [33, 34]. The purpose of the present work is to investigate the effects of Er-doped (0, 0.02, 0.1, 0.2 and 0.5 mol%) on CCTO ceramics in the room temperature using sol-gel method. Normally, CCTO is synthesized by a mixed-oxide reaction method. However, the powders prepared by this method usually exhibit a high agglomeration and an inhomogeneous particle size, thus requiring a subsequent high-temperature treatment. The sol-gel method is a chemical solution process. In comparison with other techniques, the sol–gel process has shown considerable advantages, including excellent chemical stoichiometry, compositional homogeneity and lower crystallization/sintering (processing) temperature due to the mixing of liquid precursors on the molecular level [35-37]. In our synthesis process, acetic and citric acid were used as the chelating reagent. B. Shri Prakash et al., [38] reported that the dielectric constant (Ɛr) of $CaCu_3Ti_4O_{12}$ decreased drastically on La doping, the Ɛr value at 100 kHz was about 1700. In this investigation Er 0.5% doping the dielectric constant was raised to 11,700 for 50 Hz.

This paper reports the details microstructural and dielectric properties of Er doping on titanium site in the CCTO ceramics synthesized by sol-gel method followed by microwave sintering. The results revealed that Er doping ions have significant influences on microstructural and dielectric properties. The possible mechanisms related to these observations are discussed.

MATERIALS AND METHODS

$CaCu_3Ti_{(4-x)}Er_xO_{12}$ abbreviated as CCTEO [x = 0, 0.02, 0.1, 0.2, 0.5 and 1.0] powders were prepared by sol-gel method using Ca $(NO_3)_2\cdot 4H_2O$, Cu $(NO_3)_2\cdot 3H_2O$, Er(NO) $_3$and $C_{12}H_{28}O_4Ti$ as raw materials. Calcium nitrate and copper nitrate were dissolved in ethanol (solution1). Titanium tetra isoproxide stabilized by acetyl acetone was dissolved in isopropyl alchocal, Erbium nitrate dissolved in ethanol was mixed (solution2) with this solution. These two solutions were mixed in a beaker and stirred continuously using a magnetic stirrer at room temperature. Acetic acid and Citric acid added slowly into this solution and the temperature was slowly raised to 90 °C to form gel. The glacial acetic acid and citric acid were the chelating reagent. The transparent sol with blue color was obtained after stirring and hydrolyzing the mixture solution. When the mixture was concentrated the viscous liquid transformed into a transparent gel. Finally, the dried gel was dried at 110 °C for 2 days. Subsequently, the dried precursor was calcined at 800 °C, for 3 hrs for crystallization and the milling process was carried out in order to get a nano powder.

X-ray powder diffraction (XRD) studies were carried out with an X'PERT-PRO Diffract meter (Philips, the Netherlands) using Cu Kα1 radiation at 45 kV and 40 mA (λ = 0.154056nm) in a wide range of 2θ ($5° < 2\theta < 85°$). The calcined powder was uniaxially pressed into pellets of 10mm in diameter and 2mm in thickness with an applied load of 3.5 tons for 4 minutes, using poly vinyl alcohol (PVA) as the binder. The green pellets were then sintered at 1000 °C for 10 minutes in a microwave furnace. The microstructure of sintered pellets was observed by FE-SEM (FEI Quanta 200FEG). Silver paste was coated over the parallel faces of the pellets and the dielectric constant [39] measurements were made using LCR meter (Hioki 3532-50) in the frequency range of 50 Hz -1 MHz at room temperature

RESULTS AND DISCUSSION

3.1 X-ray diffraction pattern of calcined $CaCu_3Ti_{4-x}Er_xO_{12}$ powder

Figure 1 shows the XRD patterns [40] of pure and Er-doped CCTEO ceramics with different doping concentrations (x = 0, 0.02, 0.1, 0.2, 0.5 and 1.0) calcined at 800 °C for 3 hours. The CCTO main peaks and those of Er doped CCTO powders were compared with the standard powder diffraction pattern (JCPDS card No: 75-2188). The major planes corresponding to (211), (220), (013), (222), (400), (422) and (440) were found to be matched with Cubic $(CaCu_3)$ Ti_4O_{12}. From the XRD pattern it was found that the concentration of Erbium doped with CCTO was within the limit of its solubility up to x=0.2 and hence there was no second phase. When x=0.5 and 1.0, all the main peaks were matched and extra peaks are present corresponded to Erbium oxide which indicates the excess amount of erbium which is not within the limit of its solubility.

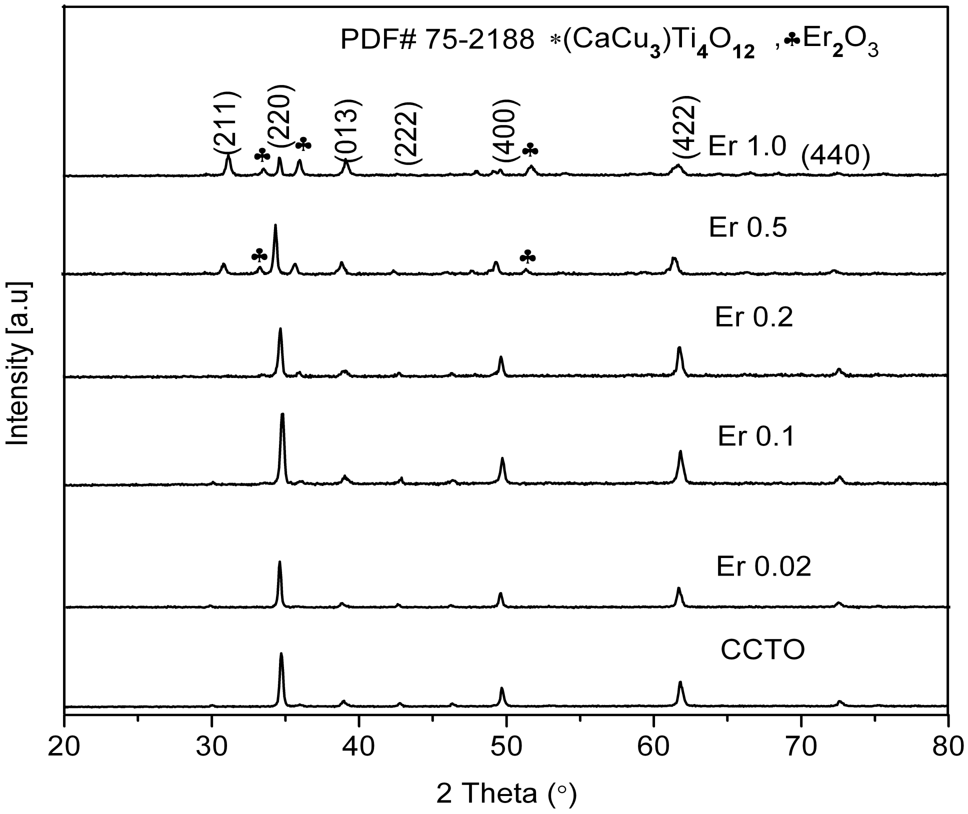

Fig. 1: XRD patterns of CCTO powder calcined in air at 800 °C and $CaCu_3Ti_{(4-x)}Er_xO_{12}$ (x = 0, 0.02, 0.10, 0.20, 0.50and 1.00) calcined at 800 °C for 3hrs

3.2 FE-SEM analysis

The $CaCu_3Ti_{(4-x)}Er_xO_{12}$ [x= 0,0.02, 0.1, 0.2, 0.5 and 1.0] ceramics, microwave sintered at 1000 °C for 10min, is as shown in Fig .2. [a-.f]. The grains are found to be cubic and had spherical shape with the range size of 250 nm–3µm. An obvious change in size and shape was observed after Er-doping. Microstructure [41] of the samples showed a matrix consisting of large grains wherein the small grains were embedded between the larger grains. In the x = 0.02 doped sample it is seen to have grains and pores of almost the same size like undoped sample (Fig. 4b). When the concentration of Er dopant x corresponds to 0.1; the grains are almost same but the some of the grains size are reduced. The microstructure (x=0.2) showed a matrix consisting of large grains wherein the small grains were embedded between the larger grains. The porosity present in the samples was intergranular in nature. An increase in the dopant level (0.5 and 1.0) leads to a decrease in shape and size of the grains and the structure appears to be porous. S. Jesurani et all., [42] reported an obvious change in grain size and its shape with higher level doping (0.1 mol% and above) in CCTO. From their results, increase in dopant level illustrates pebble to sphere and sheet-like grains, surrounded by blurry grain boundaries which may be caused by the excess liquid composed of oxide phase of dopant during high temperature sintering. Thomas et al. reported that dielectric properties of CCTO ceramics have shown a strong dependence on microstructure [43]. From the previous published report, the increasing Erbium concentration changed the shape of particles from spherical to polyhedral dimensions [44]. The Energy dispersive X-ray (EDX) spectra for the composition of x = 0.1 is shown in Fig.2 (incet 2f). This spectrum confirms the presence of erbium in CCTEO ceramics.

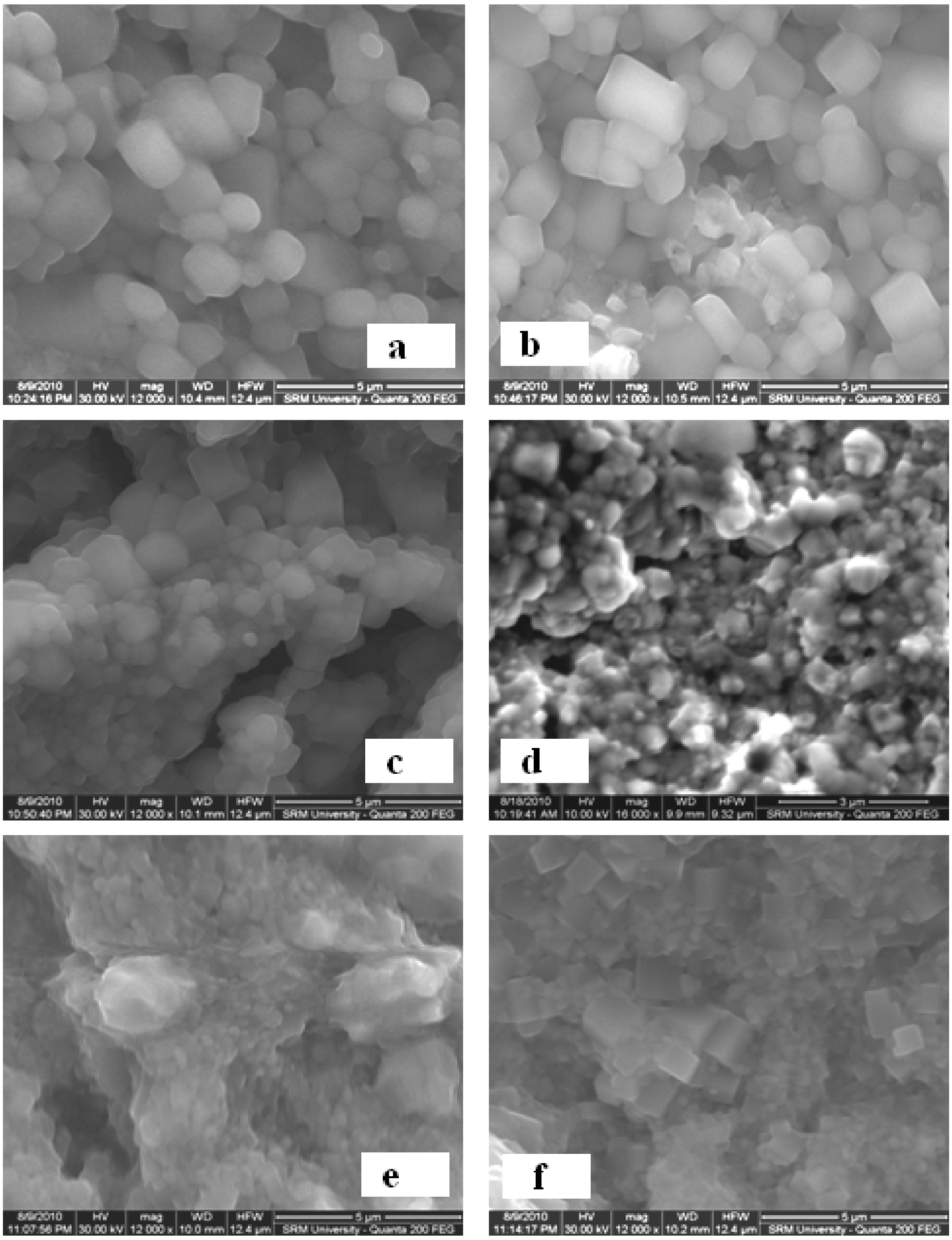

Fig. 2: FE-SEM micrographs of $CaCu_3Ti_{4-x}Er_xO_{12}$: (a) CCTO (b) 0.02 (c) 0.10, (d) 0.20, (e) 0.50 and (f) 1.00 microwave sintered at 1000 °C -10min

3.3 Dielectric studies

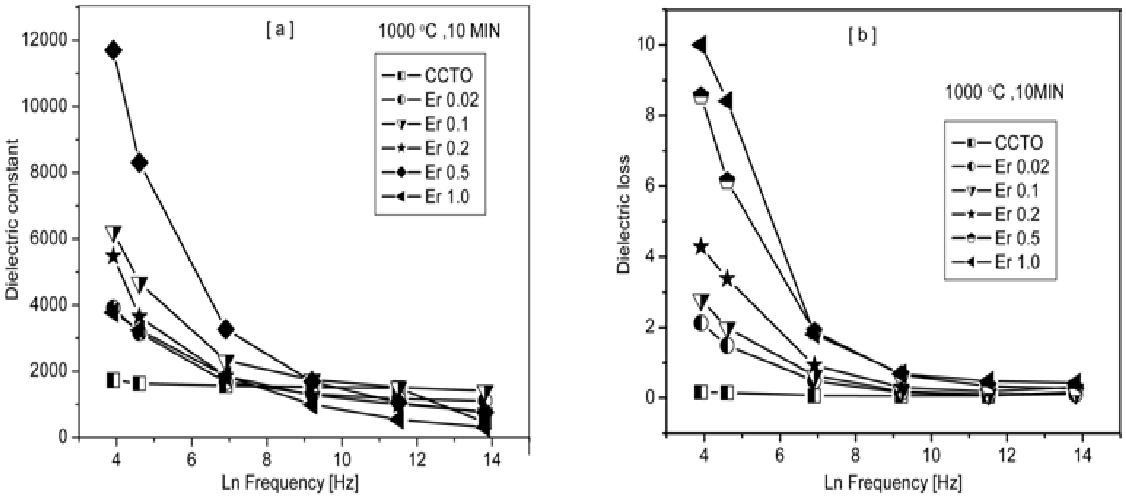

Fig. 3 Frequency dependence of the dielectric constant and dielectric loss of Er-doped CCTO ceramics sintered at 1000 °C-10min using microwave

Table. 1 Dielectric constant and loss of CCTO and Erbium dopants using microwave sintering at 1000 °C for 10min

Frequency HZ	**x = 0**		**x = 0.02**		**x = 0.1**		**x = 0.2**		**x = 0.5**		**x = 1.0**	
	ε_r	**tan δ**	ε_r	**tan δ**	ε_r	**tan δ**	ε_r	**tan δ**	ε_r	**tan δ**	ε_r	**tan δ**
50	1730	0.16	3910	2.1	6220	2.7	5480	4.2	11,700	8.5	3780	9.9
100	1633	0.15	3170	1.4	4680	1.9	3650	3.3	8310	6.1	3250	8.4
1k	1572	0.06	1680	0.4	2320	0.6	1850	0.9	3270	1.8	1850	1.8
10k	1527	0.06	1310	0.1	1750	0.1	1280	0.3	1690	0.6	996	0.6
100k	1491	0.06	1170	0.08	1520	0.09	1010	0.1	1050	0.3	545	0.4
1m	1462	0.17	1110	0.1	1410	0.1	790	0.3	762	0.2	313	0.4

The dielectric properties for Erbium doped microwave sintered samples at 1000 °C for 10 minutes is shown in Fig.3 and Table. 1. The high dielectric constants of these samples are 1730, 3910, 6220, 5480, 11,700, and 3780 and the corresponding dielectric losses are 0.16, 2.1, 2.7, 4.2, 8.5 and 9.9. 0.5). The mentioned values are higher than the pure CCTO in the low-frequency range [45] and even lower in the high-frequency range. However, the dielectric constant of pure CCTO ceramic is almost constant through the whole frequency range with a lower ε_r value. The lower concentrations of erbium x = 0.02 to 0.1 the dielectric constant was found to increase from 1110 to 6220. The dielectric constant decreased at the concentration of erbium x = 0.2. The dielectric constant for Erbium doped x = 0.5 again increased. The higher concentration of erbium (x = 1.0), the dielectric constant was found to decreases. Dielectric loss was found to continually increase with the increasing erbium concentration (0.1 to 9.9). From the results, one can observe that the highest dielectric constant (11,700) is obtained when the concentration value of x is 0.5. The dielectric constant drops from 11,700 at the frequency of 50Hz to 762 at the frequency of 1.0 MHz. The dielectric loss varies from 8.5 to 0.20 for 50Hz to 1MHz. The high dielectric constant at low frequency region suggests the possibility that the charge carriers accumulate at the interface of semiconducting grains and insulating grain boundaries, which results in interfacial space charge polarization. As the frequency increases, the shift in the maximum dielectric constant shifts towards lower concentration of Er. It is noted that the samples are polycrystalline and therefore differ in the relative density of grain boundaries. Such a difference could affect the dielectric constant via the boundary layer mechanism. Electrical heterogeneity originating from the mobile charged species and the internal interfaces in polycrystalline CCTEO gives rise to the polarization in semiconducting grains and insulating grain boundaries [46, 47]. The grain boundary in-homogeneity was confirmed by the existence of electrical potential barriers via current–voltage measurements. So far, the internal barrier layer capacitor (IBLC) model has been widely accepted as the most likely mechanism to elucidate the high dielectric constant in CCTO.

S. Choudhury et al., [48] have reported that the dielectric constant of Zr doped $BaTiO_3$ samples prepared by high temperature solid state reaction at a sintering temperature of 1250° C showed a maximum value of about 1000 for 100 kHz. C. Gomez-Yanez et al., [49] have also reported that the dielectric constant and dielectric loss are 576, 0.33 respectively. When Zr doped $BaTiO_3$ is synthesized by mechanical alloying [49], its dielectric constant is 539;

however, when the sample is sintered in the range of 1200-1400°C, as in the present investigation, a much higher dielectric constant (11,700) is obtained. The sintering temperature is on or above 1100 °C [15, 43, 50, 51] in most of the recently published investigations, which has been brought lower (1000°C) in the present work.

CONCLUSION

In conclusions, substitution of the rare earth trivalent dopant Er on the Ti site was investigated at doping concentration of x= 0.02-1.0. No evidence of secondary phases was observed from XRD analysis. XRD studies indicated the structure of $CaCu_3Ti_{(4-x)}Er_xO_{12}$ [x = 0, 0.02, 0.1, 0.2, 0.5 and 1.0] to be cubic. Microstructure shows that grains have size in the range of 250 nm–3 µm. Energy dispersive X-ray spectroscopy for the ceramics [x = 1.0], confirmed the presence of Erbium. The microstructure study shows that the increasing erbium concentration above x > 0.1 changes the shape of grains. From these results, x = 0.5 mole % concentration is an efficient to achieve a high-dielectric constant.

Acknowledgements

We would like to thank SRM University for providing the Nanotechnology center Facilities and ITMA, Universiti Putra Malaysia for the pre-submission final editing of this paper.

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