

# Preparation and structural properties of multi-phases Nanocrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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## Abstract

Nanocrystalline multiphase  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was prepared using  $\text{CaNO}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuNO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{TiO}_2$  and oxalic acid. Effect of pH has been studied from the phase formation behavior of the CCTO powder wherein the pH was varied 3, 5, 6, 7, 8, and 11. It is found that the multiphase are content a  $\text{TiO}_2$ ,  $\text{CuO}$ ,  $\text{CaTiO}_3$  and CCTO as shown on XRD result. The crystallite size was about 60 nm according to XRD result using Scherrer's equation. The color of prepared (CCTO) powder was light blue at room temperature, then it changes to brown and dark brown when annealing at  $800^\circ\text{C}$  and  $900^\circ\text{C}$  respectively which can attributed to demerit second phase. Carbonate groups were observed in the prepared powder calcined  $900^\circ\text{C}$  at pH equals to 6 and 7 that showed at FTIR spectroscopy as a vibration peaks. These groups were not showed in powder calcined  $900^\circ\text{C}$  at pH equals to 5. FTIR and XRD results have confirmed that the pH value for preparing multi phases CCTO is 5.

## Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) is possessing high dielectric constant and nearly constant at room temperature to  $300^\circ\text{C}$ . CCTO was reported to hold a giant dielectric constant ( $10^5$ ) at room temperature under varies frequencies and show small temperature dependence around this temperature range[1]. Both properties are very important for application of dielectric device development. It is being widely used in the electronic industries to manufacture electronic components such as multilayer capacitor (MLCC), DRAMs, microwave devices, electronic devices in automobiles and aircrafts embedded sensors and electric energy storage devices [2,3]. The high permittivity of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  depends upon the particle size and powder morphology, which depend on the different processing parameters such as temperature, heating rate, duration and

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atmosphere [4]. Different hypotheses have been to explain the high dielectric constant of CCTO. One of them depends on the formation of an internal layer capacitor between semi conduction grains and insulating grain boundaries [5].

The structure of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is derived from the cubic perovskite ( $\text{ABO}_3$ ) by an octahedral tilt distortion caused by size mismatch and the nature of the A cations [ 6]. The  $\text{TiO}_6$  octahedra tilt to produce a structure where three-quarters of the A sites have square–planar coordination and are occupied by Jahn–Teller  $\text{Cu}^{2+}$  ions [7]. The remaining quarters of the sites occupied by Ca and have 12 fold coordination . CCTO has attracted a huge amount of work to understand the origin of its dielectric properties[8].

CCTO is prepared by different method, the solid state synthesis[8], Sol-gel method [9,10], pulsed laser deposition[11], chemical layer deposition[12], and precursor oxalate route[9,12].

The traditional solid state reaction is the general used to prepare CCTO. The disadvantage of this method is including non uniformity, limitation of particle size, and needing high sintering temperature with long time ( $1100^\circ\text{C}$  at 24 hours)[13].

The quick, safe, and low cost route takes the advantage of the formation of CCTO is a chemical method[13].

The present paper reports the synthesis of CCTO nano powder using oxalate method. The effects of pH value, sintering temperature and structure of CCTO powder have been investigated[12,13].

### **Experimental**

CCTO nano powders were prepared by oxalate method. The starting materials  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{TiO}_2$ , and oxalic acid, were used to prepare CCTO nano powder. Stoichiometric amount of  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were mixed distilling water for one hour.

An appropriate amount of  $\text{TiO}_2$  was dissolved in oxalic acid using ultrasonic path for 10 min. The mixing of nitrates was dropped into dissolving  $\text{TiO}_2$  and adjusted pH at 3,5,6,7, 8 and 11 using ammonia. The result was filtering and washing with dionized water, ethanol and hot water for many times to remove any excess unwanted ions. The result powder calcined at  $800^\circ\text{C}$  and  $900^\circ\text{C}$ . The oxalate method depends on the super saturation of solution. In the present work, the heterogeneous super saturation was adjusted using the dilute solution.

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The crystalline phase was identified by powder X-ray diffraction analysis with  $\text{Cu } k_\alpha$  radiation (XRD- 6000). The prepared CCTO powers were characterized by Fourier transform infrared spectrometer (Spectrum One FT-IR Spectrometer, PerkinElmer Instruments, USA).

### **Result and Discussion**

Fig 1 depicts the color of the calcined powder at  $800^\circ\text{C}$  with pH equal to 3, 6, and 8. The color of prepared powder is light blue, then transformed to brown and dark brown after varying pH at 3, 6, and 8 respectively as shown in Fig 1.

The degree of crystallinity and phases were tested by X-ray diffraction. Fig 2 shows that the powders heat treated at  $800^\circ\text{C}$  for 1h with varying pH to 3, 6 and 8. At pH equal to 3 (Fig 2a)  $\text{TiO}_2$  and  $\text{CuO}$  were the main phases present, followed by CCTO and  $\text{CaTiO}_3$ . The  $\text{TiO}_2$  is present both in the anatase and in the rutile phases. Varying the pH to 6 as shown in Fig 2b leads to dominate the peaks of CCTO with some extra of peaks which might be attributed to react the excess Titania. At pH 8, the main peaks return to belong to the secondary phases (Fig 2c). Excess  $\text{CaO}$  peaks were not clearly observed in the XRD results, possibly due to reaction to form CCTO. The main peaks of calcined CCTO powders are compared with standard powder diffraction pattern (JCPDS card No. 75-2188). The main peaks of secondary phases are compared with JCPDS card No. 78- 2485 for rutile  $\text{TiO}_2$ , JCPDS card No. 75- 2486 for anatase  $\text{TiO}_2$ , JCPDS card No. 81- 0561 for  $\text{CaTiO}_3$ , and JCPDS card No. 80-1917 for  $\text{CuO}$ .

The intensity ratios of secondary phases as a function of pH values of the powders heat treated at  $800^\circ\text{C}$  are shown in Fig 3. At pH equal to 3,  $\text{TiO}_2$  and  $\text{CuO}$  peaks were dominated. With increasing pH to 6 these peaks were decreased then increased at pH increased to 8 as shown in Fig 3. The intensity ratio of  $\text{CaTiO}_3$  peaks to CCTO peaks is same behavior of  $\text{TiO}_2$  and  $\text{CuO}$  except the depressing the curve of it. The XRD results confirm that the formation of pure single crystalline CCTO is obtained at pH value between 5 and 7 and at temperature above  $800^\circ\text{C}$ .

Fig 4 shows a color of calcined powder at  $900^\circ\text{C}$  with varying pH at 3, 5, 6, 7, 8, and 11 respectively. It can be seen that the dominion of secondary phases is responsible to the change of color's powder.

Fig 5 shows that the XRD result of powders heat treated at  $900^\circ\text{C}$  for 1 h with different pH values. The second phases ( $\text{TiO}_2$  and  $\text{CuO}$ ) are gradually decreases with increasing heat treated powders at  $900^\circ\text{C}$  for different values of pH from 3 to 11 as shown in Fig 5. There is no different between XRD result of powders which heat treated at  $800^\circ\text{C}$  and

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900°C at pH equal to 3 as shown in Fig. 3a and Fig 5a. At pH equal to 5 for powder heat treated at 900°C (Fig 5b), it is clearly show that the CCTO phase is predominated with subsidence of all peaks for other phases. This can be attributed to the preparation of CCTO have been appropriated at pH equal to 5 where it is an important value to co-precipitate of Ti, Cu, and Ca compounds. At pH equal to 6 (Fig 5c), the subsidence of peaks of secondary phases were observed compared with Fig 3b. After increasing the pH values to 7, 8, and 11 as shown in Figs 5d, 3e, and 3f, the peaks of secondary phases return to predominate when compared them with peaks of CCTO. The results indicate that the powder mainly consists of CCTO crystal phase and peaks of  $\text{TiO}_2$ ,  $\text{CuO}$ , and  $\text{CaTiO}_3$  depend on the value of pH.

The intensity ratios of secondary phases as a function of pH values of the powders heat treated at 800°C are shown in Fig 6. Fig 6 indicates that there are two suitable values of pH (5 and 8), and pH equal to 5 is more accurate than 8. Average crystallite size calculated using Scherer's formula was found to be 40 nm when the powder has calcined at 900°C and it becomes 60 nm at 900°C.

To study the effect of pH for preparing multi phases CCTO, FTIR spectroscopy was investigated for different values of pH (5, 6 and 7) as shown in Fig 7. At pH equal to 6 and 7 as shown in Fig 7a and Fig 7b, there are many peaks which corresponding to O-H, C-H and  $\nu$  (M-O) stretch where M= Ti or Cu. The transmission peak corresponding to 3415 and 2937  $\text{cm}^{-1}$  is related to O-H and C-H stretching as show in spectra at pH equal to 6 and 7 (Figs 7a and 7b), only. The peak in the lower wave number 434, 514, 599, and 624 are assigned to by  $\nu$  (M-O) stretch[13] were shown in Fig 7c. FTIR and XRD results have confirmed that the pH value for preparing multi phases CCTO is 5.

### **Conclusions**

Nano-sized powders of multi-phases  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  were synthesized by an oxalate method with different values of pH and calcined at 800 and 900°C in air for 1h. The XRD results indicated that all sintered samples have a typical perovskite  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  structure with some amount of  $\text{TiO}_2$ ,  $\text{CuO}$ , and  $\text{CaTiO}_3$  as secondary phases. The ratios of intensity for secondary phases to intensity of CCTO as a function of pH values of the powders heat treated at 800°C and 900oC were confirmed that the predominate of multi-phases CCTO is agreement at pH equal to 5. According to FTIR results, it is found that the peaks in the lower wave numbers confirmed the CCTO multi-phases were formed at a value of pH is about 5.

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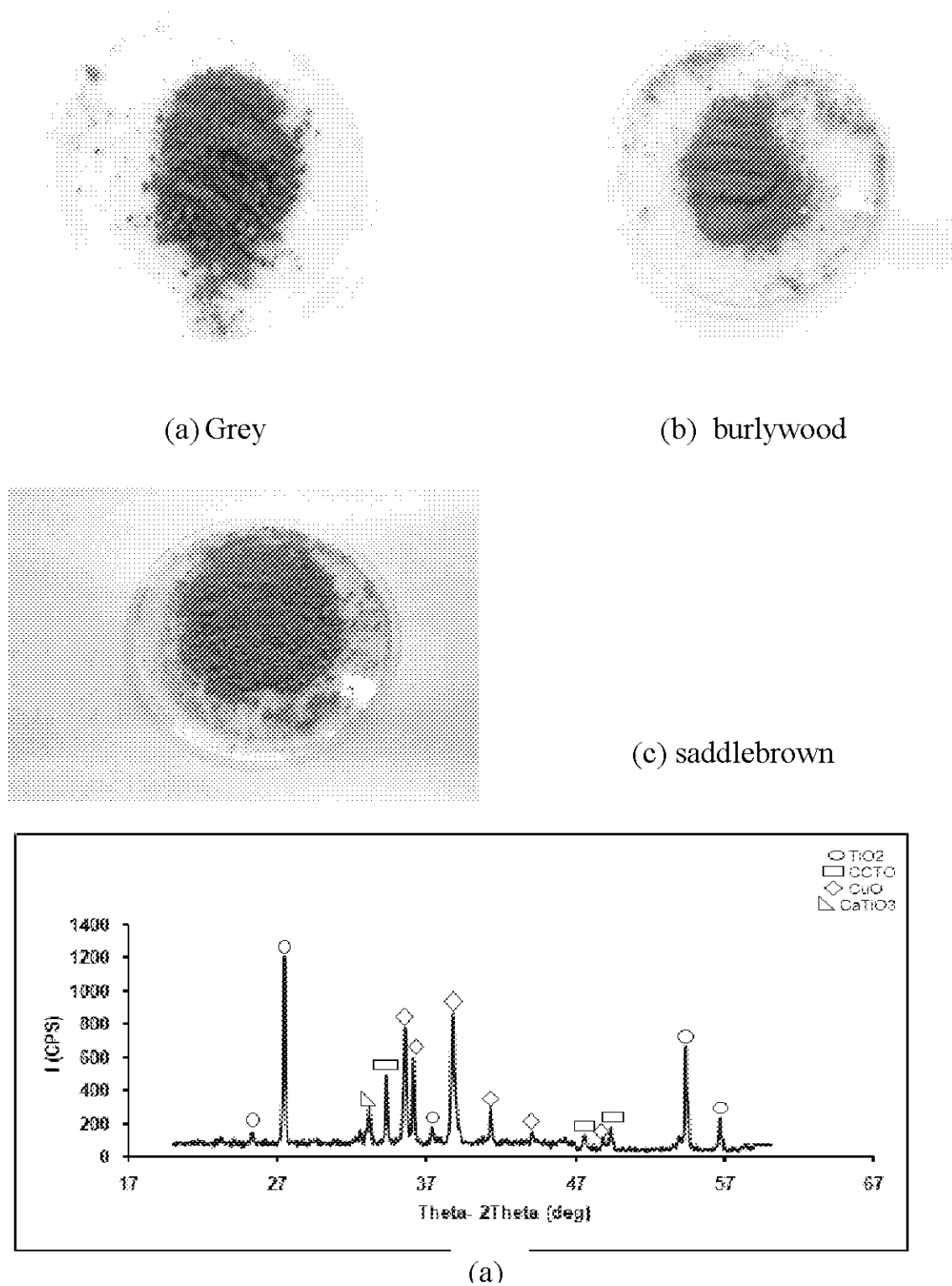


Fig 1. Color of the prepared powder with different values of pH, a) pH=3, b) pH= 6, and c) pH=8.

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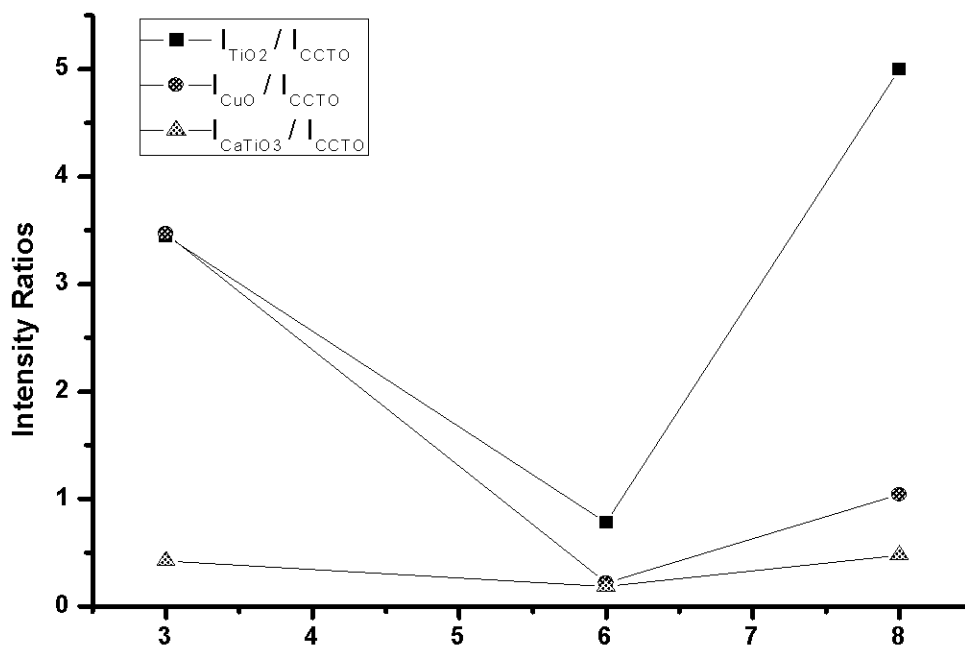


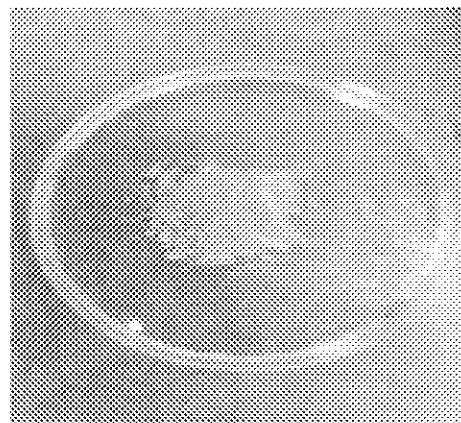
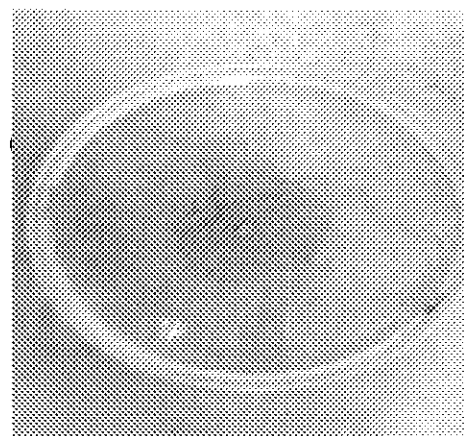
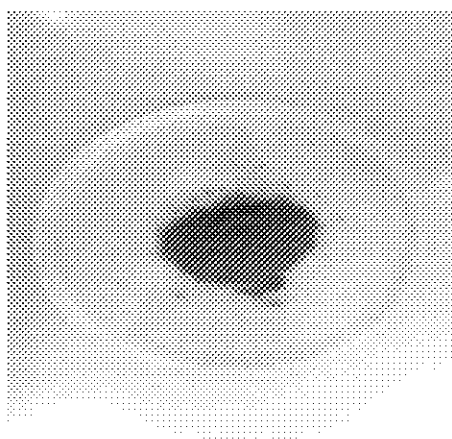
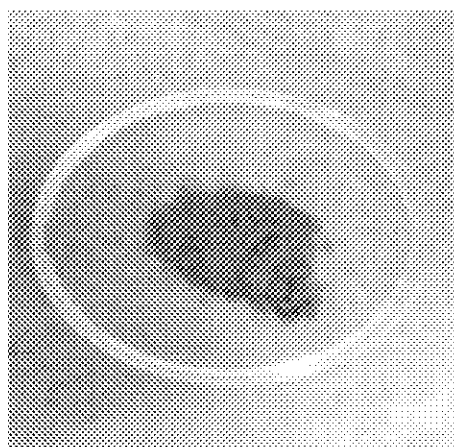
Fig 2. XRD patten of the calcined powder at  $800^\circ\text{C}$  with different pH, pH=3, b) pH=6, c) pH=8.

Fig 3. Intensity ratios of calcined powder at  $800^\circ\text{C}$  as a function of pH.

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(e)darkgoldenrod

(f) cornsilk

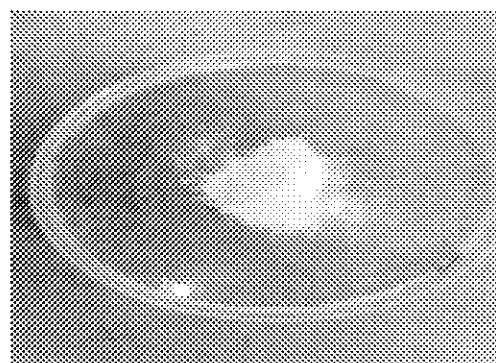
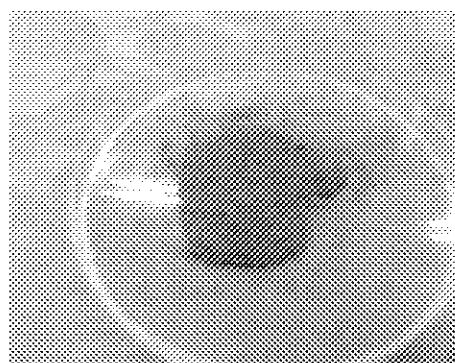
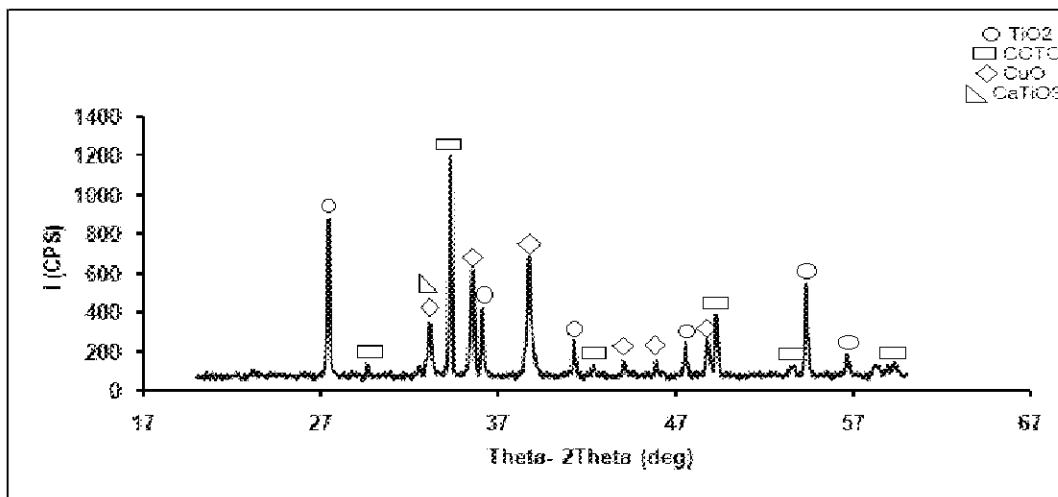


Fig 4. Color of the prepared powder with different values of pH, a) pH=3, b) pH= 5, c) pH=6, d) pH=7, e) pH=8, and f) pH=11.

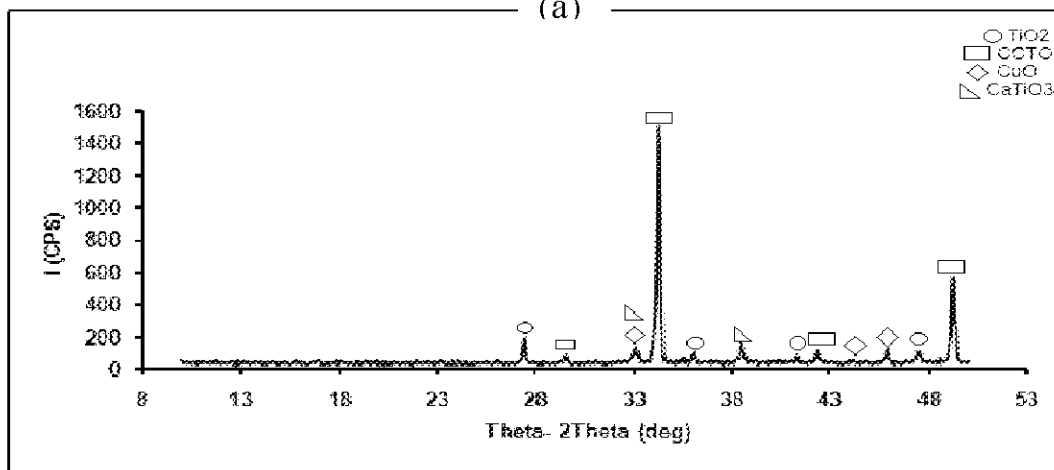


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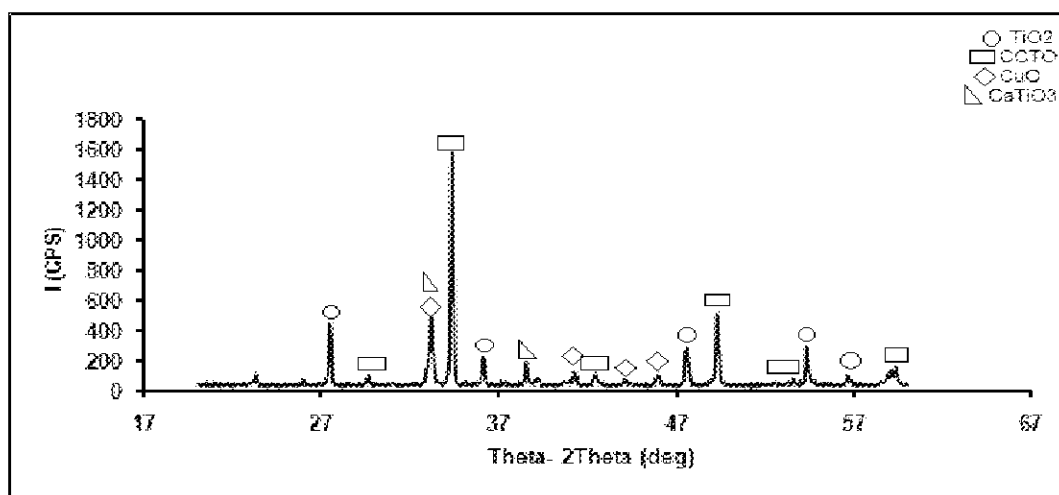
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(a)



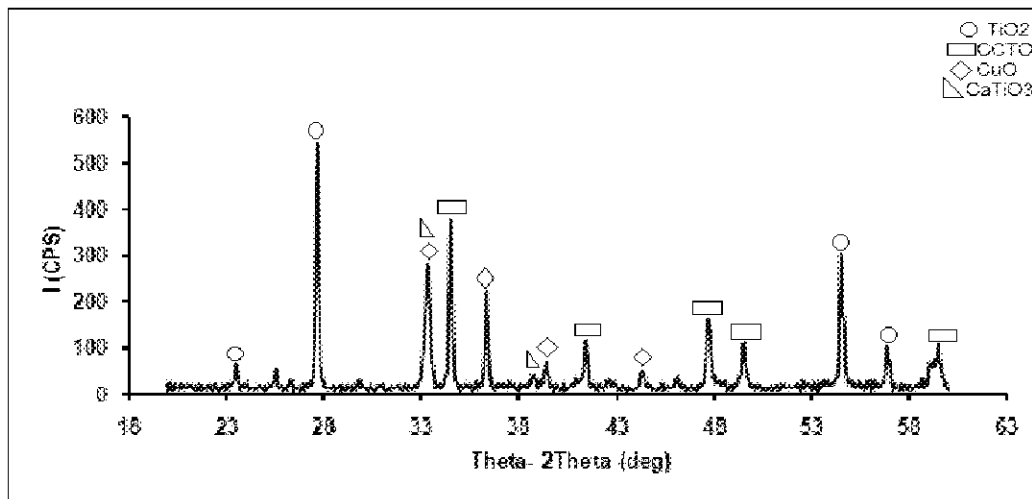
(b)



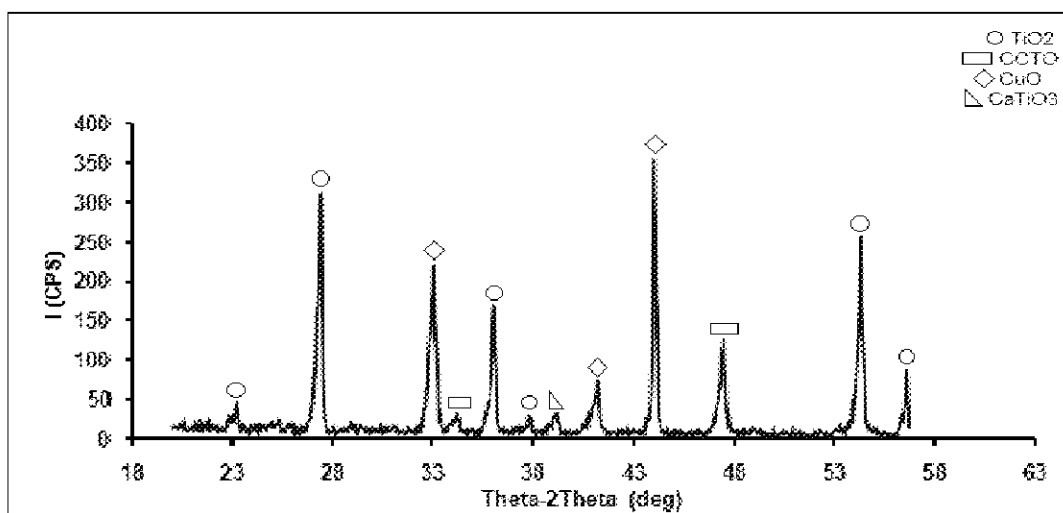
(c)

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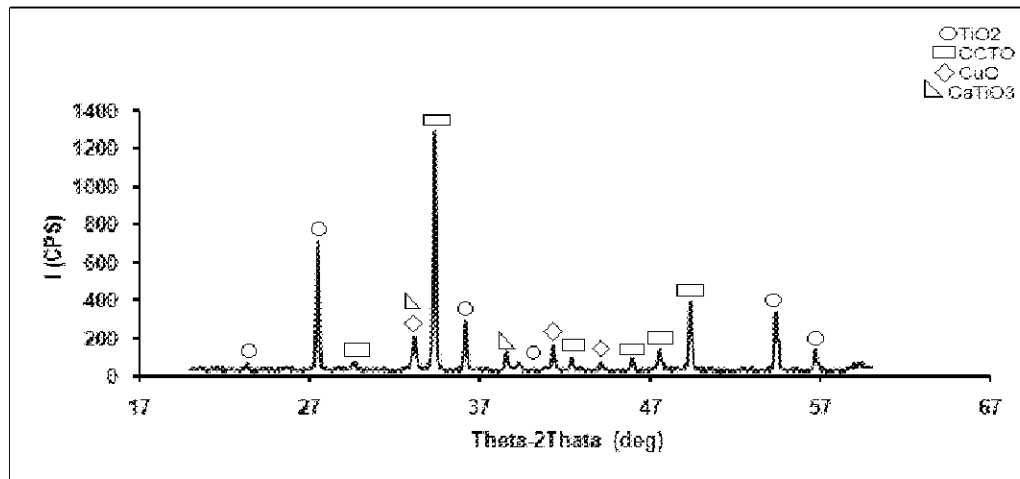
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(d)



(e)



(f)

Fig 5. XRD pattern of calcined powder at 900°C at different pH, a) pH=3, b) pH=5, c) pH=6, d) pH=7, e) pH=8, and f) pH=11.

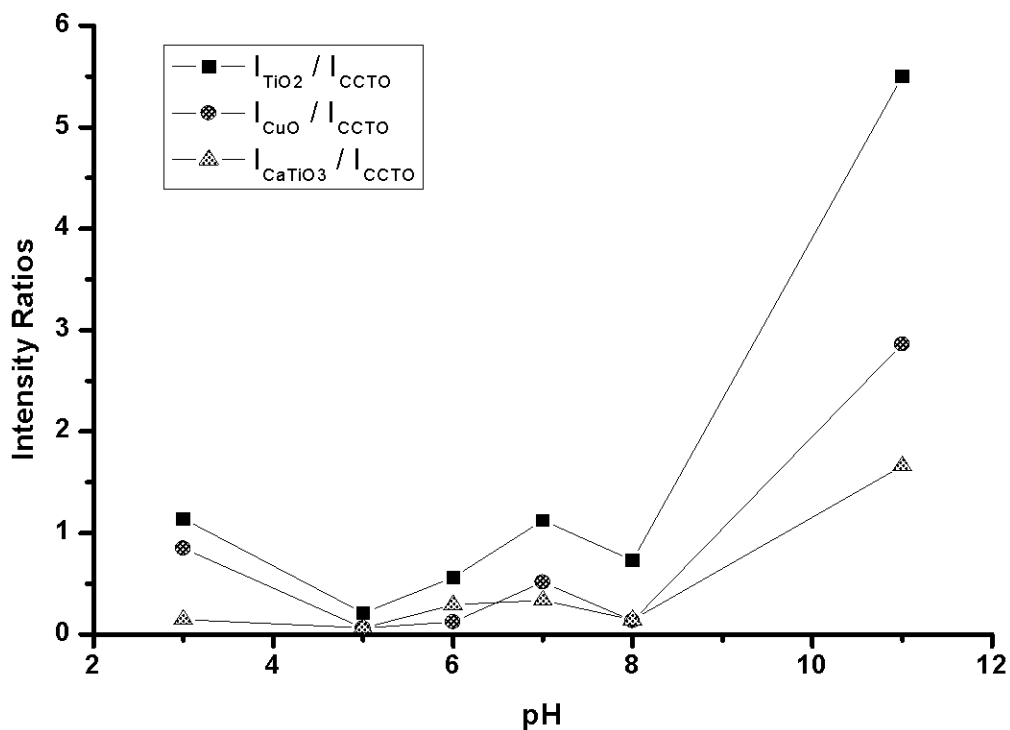
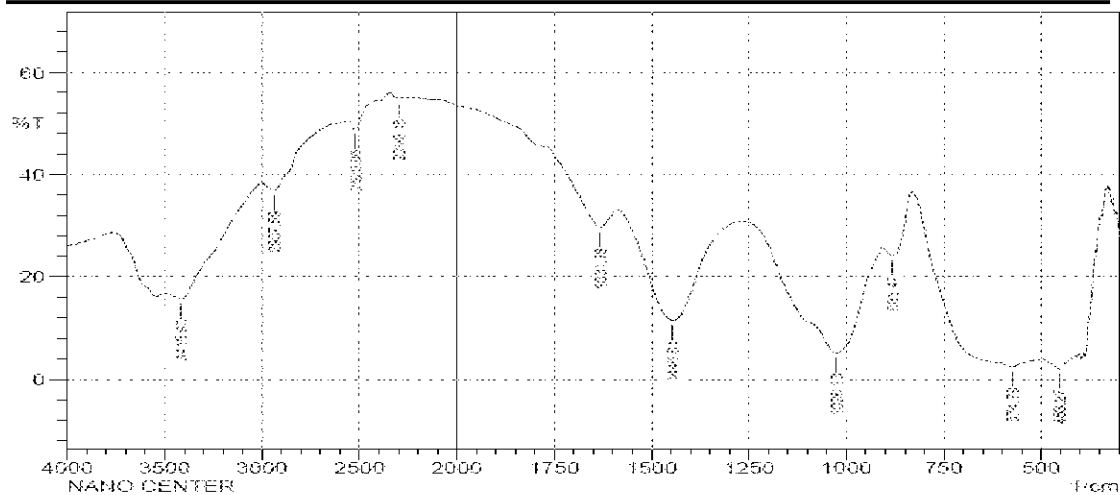


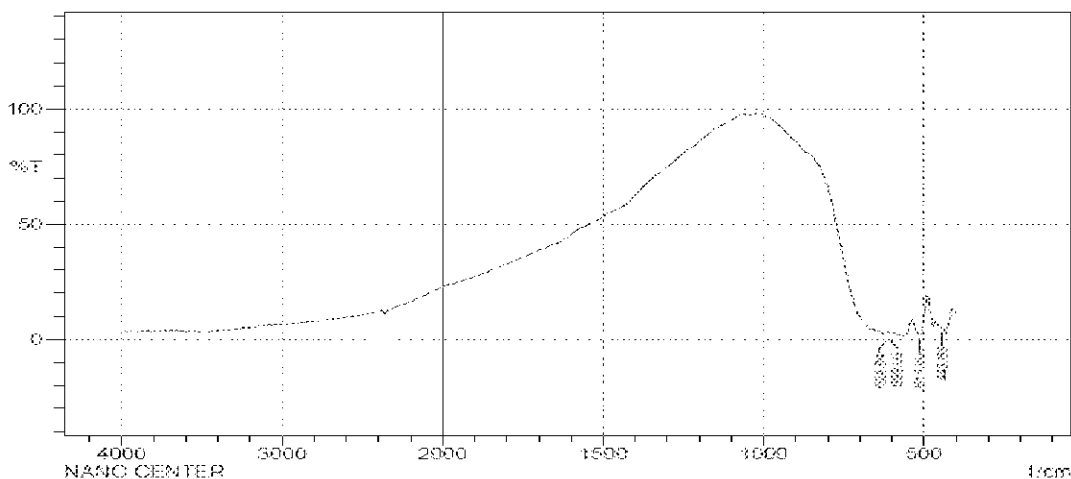
Fig 6. Intensity ratios of calcined powder at 900°C as a function of pH.

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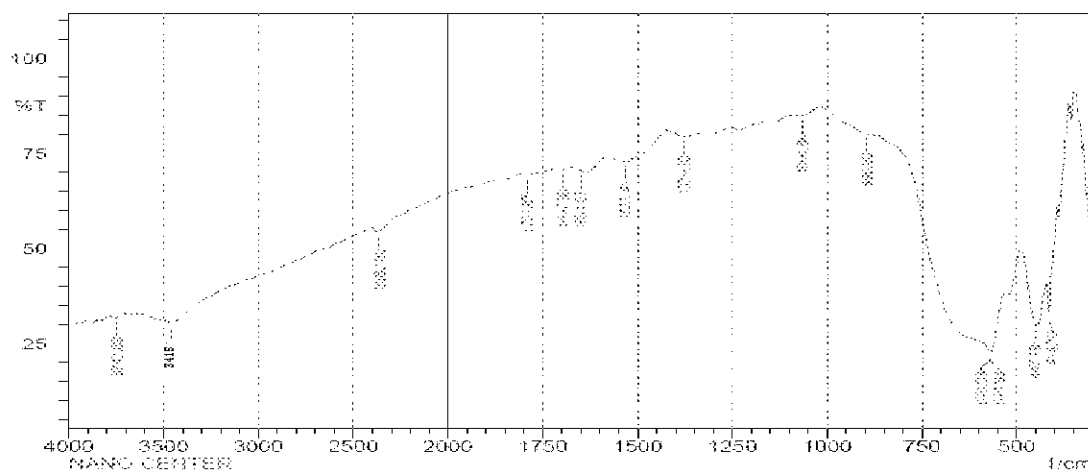
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(a)



(b)



(c)

Fig 7. FTIR spectroscopy of calcined powder at 900°C at different pH, a) pH=7, b) pH=6 and c) pH=5.