

# Crystallization and optical properties of CCTO thin films under pressure influence

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## ABSTRACT

CCTO thin films were deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si substrates using a chemical (polymeric precursor) and pressure method. The pressure effects on the CCTO thin films were evaluated by XRD, FEG-SEM and optical properties. Pressure films were found to be more homogeneous and dense than chemical deposition films. Pressure also led to an increase in the photoluminescence emission; it is suggested that the displacement of Ti in the titanate clusters, favors the charge transference from TiO<sub>6</sub> to [TiO<sub>5</sub>V<sub>6</sub><sup>2+</sup>], TiO<sub>5</sub>V<sub>6</sub><sup>2+</sup> to [CaO<sub>11</sub>V<sub>6</sub><sup>2+</sup>] and [TiO<sub>5</sub>V<sub>6</sub><sup>2+</sup>] to [CuO<sub>4</sub>]<sup>x</sup>. The low synthesis temperature used in the pressure method allows the deposition of films on less expensive substrates (i.e. glass, aluminum, polymer and others).

**Keywords:** CCTO, thin films, pressure method

## 1 INTRODUCTION

Calcium copper titanate (CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> – CCTO) has been attracted many attention and is becoming an important material to devices applications due to its high dielectric constant at room temperature (~10<sup>5</sup>) and nearly constant between 100 to 600 K [1-3]. CCTO is a variation of the perovskite structure (AB<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>) presenting TiO<sub>6</sub> octahedra clusters leading to a square planar coordination with B [4]. Perovskite structure can be considered flexible, and most distortion on this structure is based on tilting the TiO<sub>6</sub> octahedra, causing a displacement in the 180° angles of the O-Ti-O bonds [4]. The disordered structure of the perovskite contributes to PL emission at room temperature, and this effect can be observed exciting the material with wavelengths with energy higher than the band gap [5].

Photoluminescence (PL) of disordered perovskite has been studied since the first visible PL at room temperature was observed in porous silicon [6]. The order-disorder structure is one of the most concepts to explain the titanate crystalline PL emission at room temperature [7, 8]. In general, neither completely ordered nor completely

disordered systems exhibits PL; consequently a medium range order-disorder is necessary to photoluminescence emission [9-11].

In order to improve the CCTO photoluminescence emission and reduce the temperature of thin film deposition, the aim of this paper is to obtain CCTO thin films using two different methods: chemical [12] and pressure [13, 14] depositions. The influence of pressure was investigated by XRD, FEG-SEM and photoluminescence spectra. Higher PL emission and low temperature of synthesis is important to decrease the cost of several electronic and optical devices.

## 2 EXPERIMENTAL PROCEDURE

CCTO thin films were deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si substrate using a chemical (polymeric precursor) and pressure method. Calcium carbonate (Aldrich, 99.999%), copper carbonate basic (Aldrich, 99.99%), titanium isopropoxide (Aldrich, 99.999%) ethylene glycol (Synth, 99%) and citric acid (Aldrich, 99.5%) were the starting materials used in the synthesis of the CCTO polymeric solution. The viscosity of the CCTO solution was controlled to 20 cP using water and measuring with a Brookfield viscometer. Chemical films [12] (CF) were synthesized by spinning the polymeric solution on the substrate surface at 4000 RPM for 30 s, repeating this procedure layer by layer five times. CF were treated at 615 K for 32 h in order to remove the organic matter, resulting in a non-crystalline CF. The same CF were annealed at 975 K for 32 h in a conventional furnace using ambient atmosphere, resulting in a crystalline CF.

Other group of thin films was deposited by high pressure method [13, 14]. Starting from CCTO powder obtained by polymeric precursor solution, the pressure films were synthesized at 615 K with 2 MPa of pressure in air for 32 h. In order to study the pressure effect in the CCTO thin film, the CF was also annealed under high pressure system. A summary of all treatment conditions of the CCTO films is shown described in Table 1.

Films	615 K	975 K	Pressure treatment
(a) Non-crystalline CF	X		
(b) Non-crystalline CF	X		X
(c) Crystalline CF	X	X	
(d) Crystalline CF	X	X	X
(e) PF			X

Table 1. Condition of CCTO thin films deposition and treatment

CF and PF were characterized by X-ray diffraction (XRD, Rigaku, Model RINT2000) using  $\text{CuK}\alpha$  radiation in the  $2\theta$  range of  $20\text{-}80^\circ$  with  $0.02^\circ/\text{min}$  scans. The morphology of CCTO thin films were obtained by field emission gun electron microscope (FEG-SEM, JEOL, Model 7500F). Photoluminescence measurement of CF and PF were performed with a Thermo Jarrel Ash Monospec (27cm) monochromator coupled to a R955 Hamamatsu photomultiplier using krypton ion laser (Coherent Innova 200 - laser wavelengths of 350 nm); the laser's maximum output power was kept at 60 mW.

### 3 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for all CCTO thin films deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si substrate surfaces, according to the nomenclature presented in Table 1. Non-crystalline CCTO thin film (615 K) presents only substrate (platinum and silicon) reflections, indicating that 32 h of

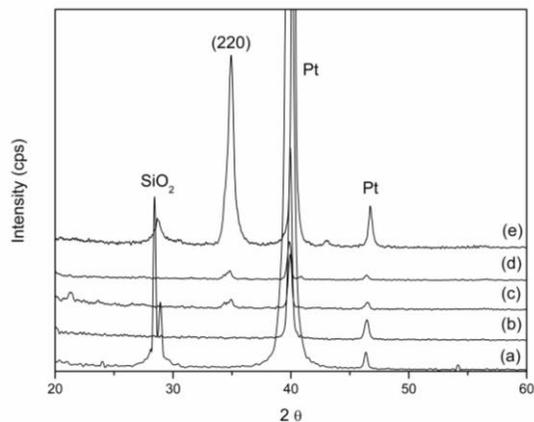


Figure 1. XRD patterns of CCTO thin film. a) non-crystalline CF, b) non-crystalline CF + pressure, c) crystalline CF, d) crystalline CF + pressure, e) pressure film

annealing treatment was only sufficient to remove the organic material, with no CCTO crystallization. In the other hand, CCTO crystalline chemical film (915 K) and pressure film (615 K and 2 MPa) show the main reflection peak of the CCTO cubic phase, which belongs to the  $Im\bar{3}$  space group (220 peak - JCPDS 75-1149).

The morphologies of the surface and cross-section of the CCTO thin films were characterized by FEG-SEM (Figure 2).

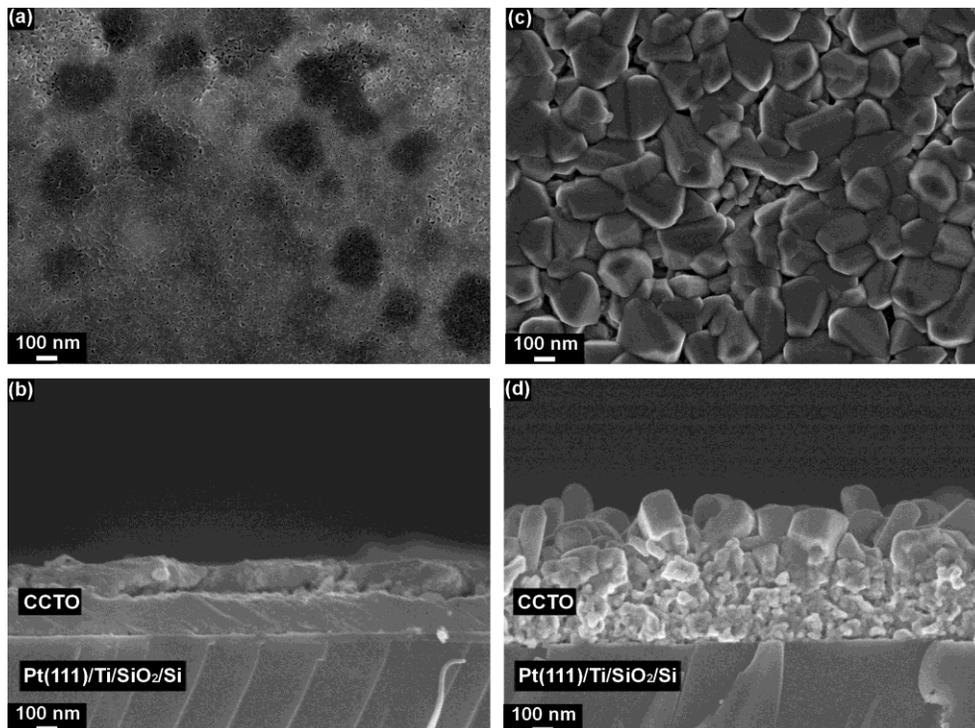


Figure 2. FEG-SEM of CCTO thin film morphologies. a) crystalline CF, b) crystalline CF cross section, c) PF, d) PF cross section.

Analyzing the surface morphology, it can be observed that PF (figure 2c) presented more homogeneous films than CF (figure 2a). Both CF and PF shows a porous surface, however PF presented larger grain (from CCTO powder) size and more dense films. Cross section micrographs show the interface film/substrate and grain size of CCTO films showing that CF grains are smaller than PF grains (figure 2 b and d, respectively). Both CF and PF demonstrated a strong adhesion with the substrate surface, and the grains of CCTO pressure film are larger especially on the top of the pressure film (figure 2d).

In order to evaluate the pressure effect on CCTO thin film structure, the photoluminescence signal for all films synthesized was studied, as can be seen in the Figure 3. As already mentioned, the photoluminescence is closely connected to the order-disorder of the material structure: short, medium and long range. CCTO is a body-centered cubic (bcc) perovskite and, the optical properties of this material are due to two main factors. The first one is related to order-disorder of  $\text{TiO}_6$  and  $\text{TiO}_5\text{V}_6^z$  clusters, in which  $\text{V}_6^z$  is the oxygen vacancies ( $\text{V}_6^x$ ,  $\text{V}_6^y$  and  $\text{V}_6^z$ ).  $\text{TiO}_6$  clusters should be linked with  $\text{CaO}_{12}$  and  $\text{CuO}_4$ , but the literature has reported that the strong green (500 to 570 nm) emission of CCTO is associated to a charger transfer from  $\text{TiO}_6$  to  $(\text{TiO}_5\text{V}_6^z)$ ,  $(\text{TiO}_5\text{V}_6^z)$  to  $(\text{CaO}_{11}\text{V}_6^z)$  and  $(\text{TiO}_5\text{V}_6^z)$  to  $(\text{CuO}_4)^x$  [5, 15]. Other authors also reported that the CCTO emission can be originated by the off-center Ti displacement along the (111) directions, which is common to  $\text{TiO}_6$  clusters [3].

More intense emission was obtained in the pressure CCTO thin film. CF film after pressure-assisted thermal annealing had the emission increased in relation to CF before pressure treatment. In both cases, the pressure was responsible for the most intense photoluminescence signal. Moreover it can be concluded that the pressure can increase the order-disorder of  $\text{TiO}_6$  cluster, increasing the off-center Ti displacement, resulting in favoring charge transfer from  $\text{TiO}_6$  to oxygen vacancies ( $\text{TiO}_5\text{V}_6^z$ ).

## 4 CONCLUSION

The use of pressure leads to improvement of PL emission in the CCTO thin films. Pressure leads to a more dense and more homogeneous films with larger grain size than chemical films. It can be suggest that the pressure-assisted annealing modified the CCTO film structure, resulting in a possible charger transfer favored by the Ti displacement in the  $\text{TiO}_6$  clusters, spearheading to origin oxygen vacancies; as a result, there is an increasing in the green emission of CCTO CF after pressure treatment and to CCTO PF. The presence of  $(\text{TiO}_5\text{V}_6^z)$  is one of the most accepted explanations of the photoluminescence of a perovskite material. The lower synthesis temperature used in the pressure method is important to allow film deposition at less expensive substrates (i.e. glass, aluminum, polymer and others), enabling to diminish the cost of some electronic devices

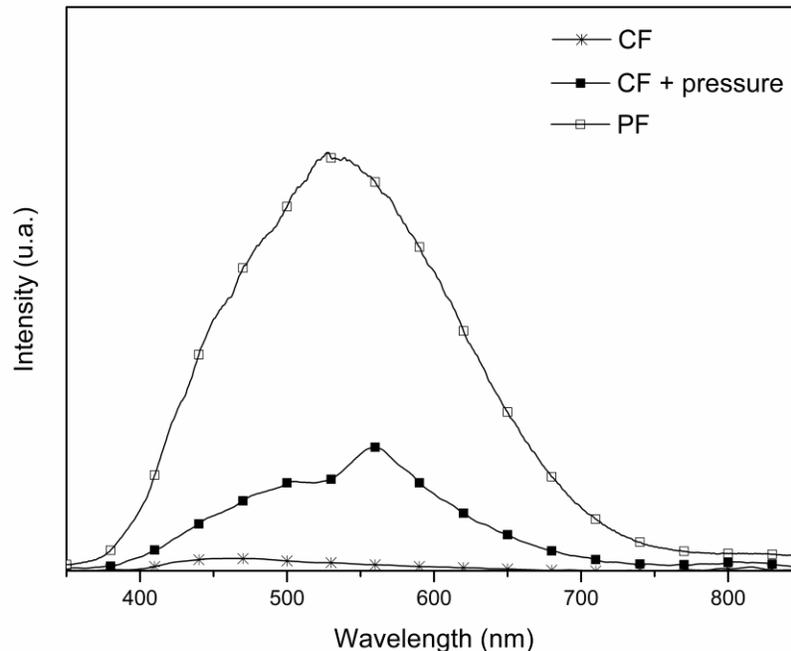


Figure 3. Photoluminescence spectra of pressure film (PF) and chemical film (CF), before and after pressure treatment.

## 5 ACKNOWLEDGMENTS

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