



ISSN : 2350-0743

www.ijramr.com



International Journal of Recent Advances in Multidisciplinary Research

Vol. 02, Issue 10, pp.0812-0816, October, 2015

## RESEARCH ARTICLE

### SUBSTITUTION OF SUBSTITUTION OF Co AND Zn IN A AND B SITES OF (PbCu) TiO<sub>3</sub>

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#### ARTICLE INFO

##### Article History:

Received 22<sup>nd</sup> July 2015

Received in revised form

12<sup>th</sup> August, 2015

Accepted 29<sup>th</sup> September, 2015

Published online 31<sup>st</sup> October, 2015

##### Keywords:

PbCuCoTiO<sub>3</sub>,

PbCuZnTiO<sub>3</sub>,

Co-doped,

The site substitution.

#### ABSTRACT

Ceramic powders of lead titanate, co-doped with copper (Pb<sub>0.9</sub>Cu<sub>0.1</sub>TiO<sub>3</sub>) and cobalt or zinc, of a perovskite structure were prepared by the sol-gel process by adopting the mode of the destabilization of colloidal solution. The effect of temperature and dopants on the structure of the obtained samples was studied by X-ray diffraction (RX), Raman spectroscopy and scanning electron microscopy (SEM). Analysis of the samples with fluorescence spectroscopy shows that Zn simultaneously occupies the sites A (Cu) and B (Ti) of the structure, creating oxygen vacancies. The effect of co-doping on the quadracity of the crystal structure was examined.

#### INTRODUCTION

Since the discovery of the perovskite structure by Russian mineralist L. A. Perovskite (Diafi, 2013), in its simple form ABO<sub>3</sub> or its complex form AB'B''O<sub>3</sub>. Pure and doped lead titanate and barium titanate are among the most studied and developed materials. Especially lead titanate families have been the subject of numerous studies, publications and thesis (Kahoul, 2013; Kighelman, 2001; Kellati, 2002; Lamcharfi, 2008), because of their interesting piezoelectric properties, nonlinear optics, optical and holographic electro. These various properties are behind many successful applications of these materials in the solid state, in the form of thin layers or as single-crystal fibers, in fields as varied as electronics (capacitors) (Bersani, 1996), ferroelectric memories (DRAM devices and NVRAM) (Lee, 1998; Joo, 1998), optics (Laud, 1969), spatial light modulators (Ishida, 1977), infrared detectors, optical waveguides, and high frequency filters. (Iijima, 1986; Okada, 1989; Li, 2008; McCaughan, 1993; Dominiak-Dzik, 1998). However the properties of lead titanate are very sensitive to the doping in site A or site B, of their perovskite structure ABO<sub>3</sub>. The role of dopants is generally to improve the properties of these materials for their adaptations to specific applications (Elmsbahi, 2006).

But, to our knowledge we have never found a study which concerns the co-doped lead titanate Cu, and Co or Zn with the following chemical formulas Pb<sub>0.9</sub>Cu<sub>0.1-y</sub>Co<sub>y</sub>TiO<sub>3</sub> and Pb<sub>0.9</sub>Cu<sub>0.1-y</sub>Zn<sub>y</sub>TiO<sub>3</sub> (y = 0, 2 and 4%). For these reasons, the co-doping effect of the latter in the matrix PT was chosen as a subject of this article. We then investigated the effect of the substitution in sites A and B on the structural characteristics of lead titanate.

#### Procedure

To elaborate the samples we used lead acetate trihydrate Pb(CH<sub>3</sub>COO)<sub>2</sub> · 3H<sub>2</sub>O, titanium alkoxide Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, cobalt acetate Co(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O, and copper acetate Cu(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O as precursors, lactic acid (CH<sub>3</sub>CH(OH)COOH) as peptizing agent, acetic acid to dissolve the acetates of cobalt. The different steps in the preparation of the Pb<sub>0.9</sub>Cu<sub>0.1-y</sub>Co<sub>y</sub>TiO<sub>3</sub> (PCuCo<sub>y</sub>T) and Pb<sub>0.9</sub>Cu<sub>0.1-y</sub>Zn<sub>y</sub>TiO<sub>3</sub> (PCuZn<sub>y</sub>T) powders are similar to those we have in other work-have shown (AElbasset, 2013).

The resultant solution was dried at 80 °C for 96h, milled in agate mortar and calcined at different temperatures for 4h to study the phase formation behavior. The crystallinity and phases of the powders were examined using X-ray diffraction (XRD) and Raman spectrum. Scanning Electron Micrographs (SEM) were obtained using a JEOLTE330 microscope. However to verify, the stoichiometry of our samples, we used Analysis of fluorescence spectroscopy.

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RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectra of pure lead titanate calcined at different temperatures. The spectrum of the powder calcined at 600 °C shows that it crystallizes in a perovskite phase with the presence of a secondary phase (lead oxide). Regarding the samples calcined at 650 and 900 °C, they show good crystallization of the powder without the presence of pyrochlore or secondary phases.

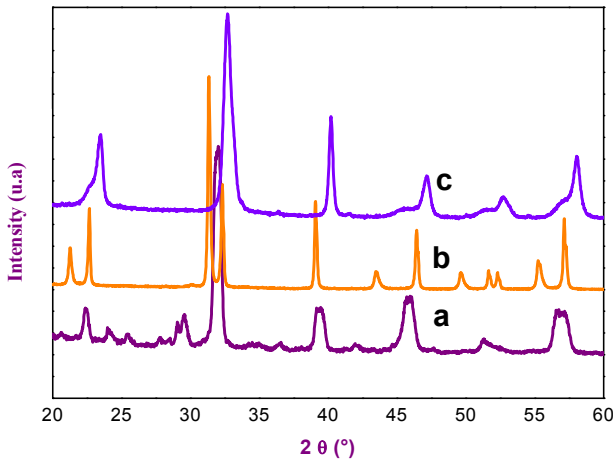


Fig. 1. PT XRD spectra calcined at 600 (a), 650 (b) and 900 °C (c) for 4 hours

In fact, the powder calcined at 650 °C shows good crystallization in the tetragonal phase (Naratip Vittayakorn, 2007; Cristiano A. Guarany, 2007; Zupei Yang, 2006). This calcination temperature is lower than the values published by several authors (Elmsbahi, 2006; Bouayad, 2005). Moreover the increase in temperature to the value of 900 °C produces a phase transformation from quadratic to pseudocubic, confirmed by the disappearance of some pics (001; 110; 102 and 201) associated with the tetragonal phase (Kellati, 2002; Shirane, 1956). According to the XRD spectra in Fig. 2, a good crystallization is observed without the presence of secondary phases. It can be also noticed an increase of the half-value width peak corresponding to the perovskite phase by increasing the amount of the doping elements in the matrix PT. More particularly, the PCu<sub>0.1</sub>T sample shows a tetragonal phase as revealed by the presence of 12 peaks between 20 and 60°. One can also observe a remarkable increase in intensity of the peaks (100) and (211); this can be explained by the difference between the ionic radii. On the other hand, the effect of addition of cobalt and zinc on the PCu<sub>0.1</sub>T structure was observed by the complete disappearance of the peak (110) together with a merging of the doublet (201)/(210).

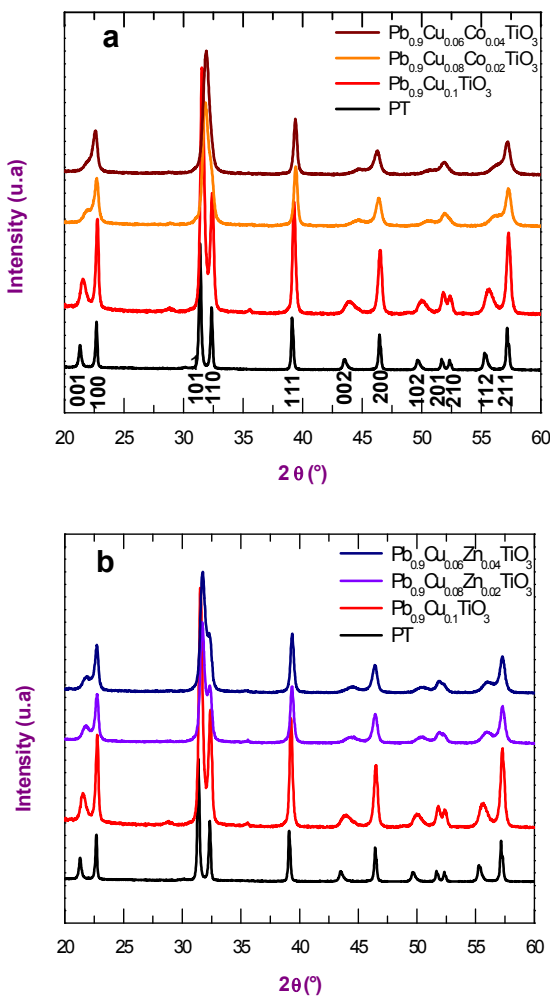


Fig. 2: Evolution of the XRD spectra of PCuCo<sub>y</sub>T (a) and PCuZn<sub>y</sub>T (b) samples calcined at 650 °C

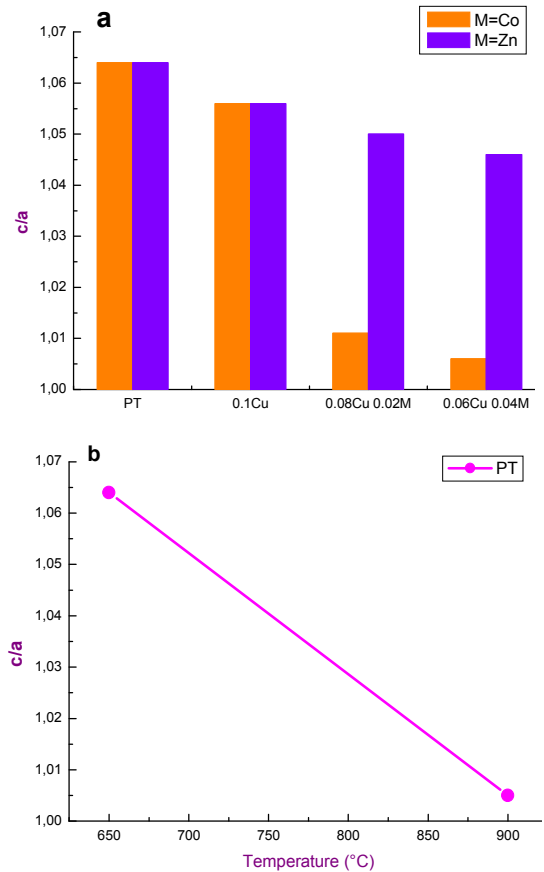


Fig. 3. Quadracity (c/a) variations for PCuZn<sub>y</sub>T and PCuCo<sub>y</sub>T calcined à 650 °C (a) and PT calcined at different temperature (b)

The spectrum of PbCu<sub>0.06</sub>Co<sub>0.04</sub>TiO<sub>3</sub> also shows the presence of a single peak at 22.5° in place of the doublet peaks (001)/(100), while this doublet is maintained in the spectrum corresponding to the sample doped with Zn (PbCu<sub>0.06</sub>Zn<sub>0.04</sub>TiO<sub>3</sub>) which characterizes the tetragonal phase; this indicates that Zn has no great influence on the structural properties of PCu<sub>0.1</sub>T compared to Co which is confirmed by the evolution of the lattice parameters as shown in Fig. 3.

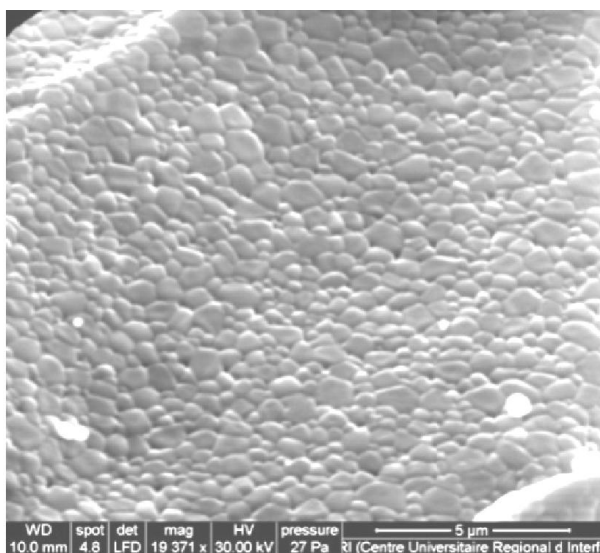
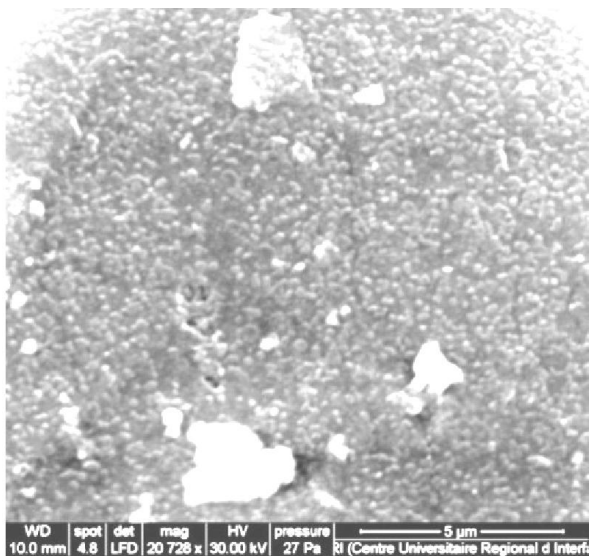
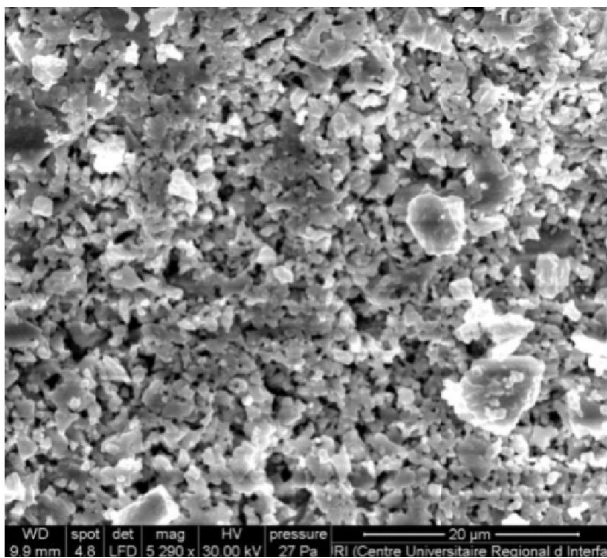


Fig. 4: SEM micrographs of PT compounds calcined to different temperatures for 4 hours

The SEM images obtained on the calcined powders for different temperatures during 4 hours (Fig. 4) show a rough surface of the powder heat treated at 600 °C with large grains of irregular and inhomogeneous shape which may be due to the presence of secondary phases.

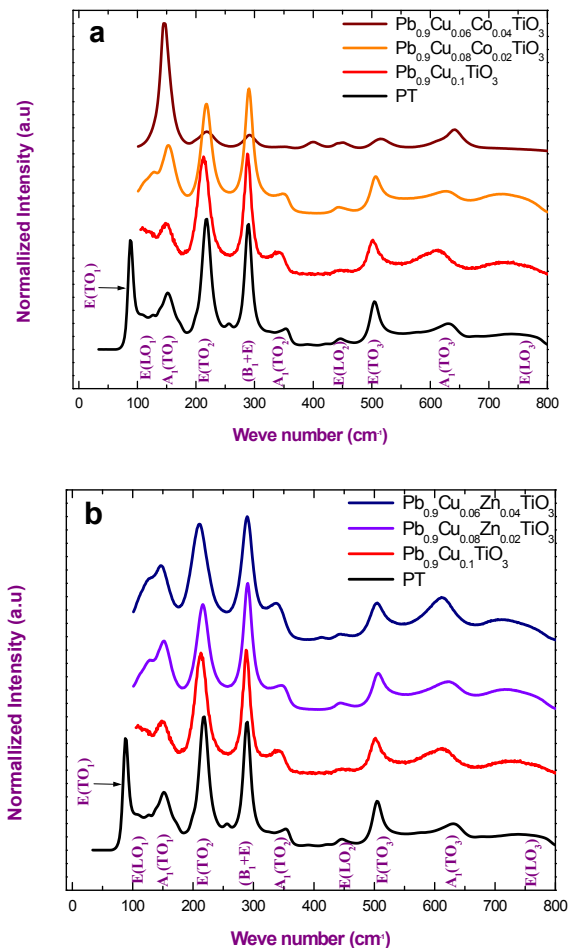


Fig. 5. Raman spectra of PCuCo<sub>y</sub>T (a) and PCuZn<sub>y</sub>T (b) heat treated at 650 °C

However increasing the calcinations temperature to 650 °C has an impact of the grains form; In fact, the grains have a relatively homogeneous and fairly regular size, and have circular or quasi-spherical form with good densification. In addition as the temperature of calcination increases the sphericity of grains increases, reflecting a new rearrangement at the mesh.

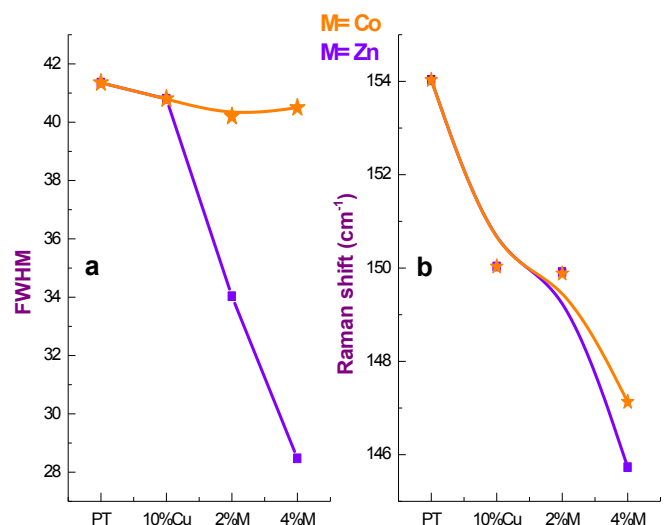
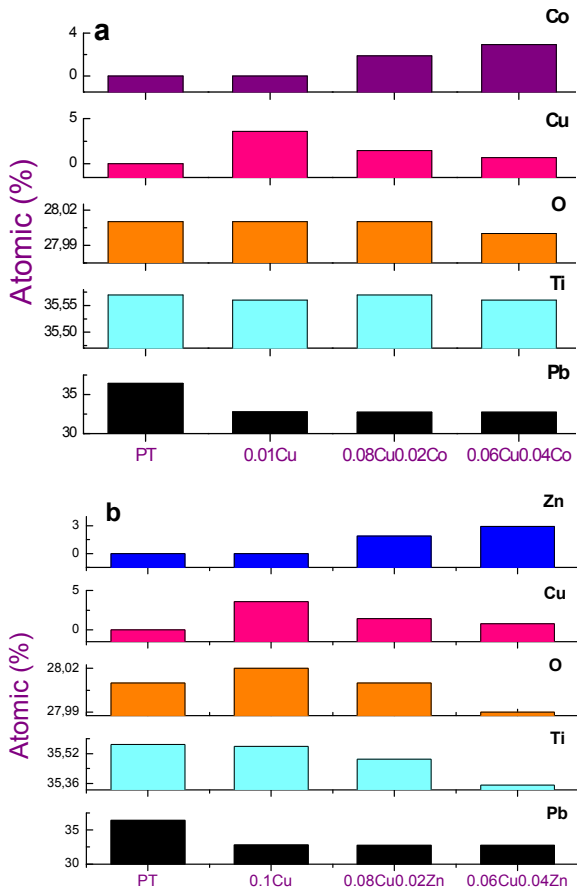


Fig. 6. The half-value width and Raman shift of the A<sub>1</sub>(TO<sub>1</sub>) mode for PCuCo<sub>y</sub>T and PCuZn<sub>y</sub>T



**Fig. 7. Analysis of fluorescence spectroscopy of PCuCo,T (a) and PCuZn,T (b)**

In addition, for 650 °C, the average grain size is about 200 nm, while the size of the powder heat treated at 900 °C is about 450 nm, this change in grain size can be explained by the coalescence of the nodules and a better crystallization, which is generally accompanied by a magnification of grains with increasing the temperature of the heat treatment, leading to more smooth and more dense surface.

The Raman spectrum of pure lead titanate PT has ten active modes between 100 and 800  $\text{cm}^{-1}$  characterizing the tetragonal phase (Burns, 1972- K. Limame, 2006). These modes are:  $E(\text{TO}_1)$ ;  $E(\text{LO}_1)$ ;  $A_1(\text{LO}_1)$ ;  $E(\text{TO}_2)$ ;  $B_1+E$ ;  $A_1(\text{TO}_2)$ ;  $E(\text{LO}_2)$ ;  $E(\text{TO}_3)$  kan;  $A_1(\text{TO}_3)$  and  $E(\text{LO}_3)$ . However, one can notice that almost the phonon modes are also present in the Raman spectra of all the doped samples. More specifically, for  $\text{PCu}_{0.04}\text{Cu}_{0.06}\text{TiO}_3$  sample, we note the decrease of the intensities of the Raman peaks  $E(\text{TO}_3)$ ;  $B_1+E$  and  $E(\text{TO}_3)$ , the complete disappearance of  $E(\text{LO}_3)$  with the displacement of the mode  $A_1(\text{TO}_3)$  to towards lower frequency positions together with an increase of its intensity. Besides, reducing the cobalt rate gives rise to an increase in intensity of almost all the modes except that of the mode  $A_1(\text{TO}_3)$ .

$\text{PbCuT}$  doping by Co causes also a merging of both modes  $A_1(\text{TO}_1)$  and  $E(\text{LO}_1)$  in a single mode positioned at 150  $\text{cm}^{-1}$  showing a significant expansion, which confirms the assumption of the phase change (G.Burns, 1972). The same tendency of evolution of Raman spectra is observed for the Zn-doped powders, however one can notice an enlargement of some phonon modes. We have represented on Fig. 6 the Raman shifts and the FWHM of the  $A_1(\text{TO}_1)$  mode for  $\text{PCuCo}_y\text{T}$  and

$\text{PCuZn}_y\text{T}$ , as this mode presents a clear signature of the induced change due to the dopant incorporation. Indeed Fig. 6.a shows that the half-value width of the  $A_1(\text{TO}_1)$  mode, representing the vibrations of the cation on the site B, remains constant up to 10% in Cu and then increases with the increase in the Zn rate. This implies that the site B of the matrix is affected by Zn.

While the FWHM of this mode for the  $\text{PCuCo}_y\text{T}$  sample remains constant, indicating that the cobalt does not affect the B site in  $\text{PbCu}_{0.1}\text{TiO}_3$ . In addition, the position of this mode shifts towards lower frequency positions with the increase in the co-doped with Co and Zn, which implies that the codoping whether by the Co or Zn affects all the Raman modes and creates a disorder on the sites concerned. To check the stoichiometry of our samples, we used a complementary analysis by the fluorescence spectroscopy. This technique has been used to ensure the stoichiometry and the possible presence of chemical elements in our  $\text{PCu}_{0.1}\text{T}$ : Co/Zn ceramics. Analysis of the results obtained (Fig. 7) shows first an increase in atomic percent of cobalt and the decrease of that of copper, showing the incorporation of Co in the  $\text{PCuT}$  in place of Cu. On the other hand, the percentage of oxygen (O) and titanium (Ti), remains relatively constant. So up to a rate of 4% Co, the latter replaces Cu in the A site of  $\text{PbCuCo}_y\text{T}$  as it was suggested. For  $\text{PbCuZn}_y\text{T}$  the results show that when the rate of Zn increases, the concentration of Cu decreases, and from 2% in Zn, Cu shows a slow decrease while Ti decreases rapidly. Furthermore, there is a significant decrease in the concentration of oxygen. This may suggest that Zn simultaneously integrates sites A (Cu) and B (Ti) of the structure, creating oxygen vacancies, and explains the relatively slight decrease of the quadracity of Zn-doped samples compared to that of Co-doped ones (Fig. 3.a). This analysis using fluorescence spectroscopy is in good agreement with Raman investigation.

## Conclusions

Using the sol-gel method, we were able to prepare samples co-doped with copper ( $\text{PCu}_{0.01}\text{T}$ ) and Cobalt or Zinc with good structural crystallization. These were crystallized at a temperature lower than that reported in the literature, namely 650 °C. However, as shown in the XRD spectra, cobalt produces a significant effect on the tetragonal phase; however, zinc keeps the tetragonal structure which is confirmed by Raman spectroscopy. Scanning electron microscopy shows that the sphericity of grains increases with decreasing the quadracity. On the other hand the fluorescence spectroscopy confirmed the incorporation of the dopants into the pure sample matrix. In addition, this study shows that cobalt replaces copper in site A while zinc simultaneously occupies the sites A and B of  $\text{PCu}_{0.01}\text{T}$  creating oxygen vacancies.

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