

Effect of Doping with Cobalt or Copper on the Structure of Lead Titanate PT

A. Elbasset^{1*}, T. Lamcharfi^{1,2}, F. Abdi^{1,2}, L. Mrharab² and S. Sayouri²

¹LSSC Department of Electrical Engineering, FST, Road Immouzer, Fes, Morocco; elbasset.abdelhalim@gmail.com

²LPTA, Physics Department, Faculty of Science DM, B.P.1796, Fes-Atlas, Morocco

Abstract

Sol gel processed $Pb_{1-x}M_xTiO_3$ (PMT_x; M = Co, 0 ≤ x ≤ 0.3; Cu, 0 ≤ x ≤ 0.2) powders, calcined at 700°C, were characterized by X-Ray Diffraction (XRD) and Raman spectroscopy. XRD analysis revealed well resolved spectra, and we have followed the influence of addition of Co and Cu with Raman spectroscopy. Indeed, the results showed that solubility limit is reached at the concentration of 10% for the samples PCuT_x, and that the structure of the samples is not significantly altered by incorporation of Cu, while addition of Co transforms it from tetragonal to pseudocubic. Moreover, Raman analysis shows that Co occupied both A (Pb) and B (Ti) sites of the ABO₃ (PbTiO₃) perovskite structure of these materials for x > 10 %, while Cu occupies the same site A (Pb) in the whole range of concentration. To our knowledge, effects of doping with Co and Cu elements and the study of sites occupation in such materials have not been reported.

Keywords: Co and Cu Doping, Half-value Width, Incorporation, PT, Raman Shift

1. Introduction

Lead titanate PbTiO₃ (PT) is a perovskite-type material (ABO₃ structure) which has received much attention due to its interesting properties: pyroelectricity, the change in polarization as a function of temperature¹, ferroelectricity, variation of the direction of polarization with the electric field^{2,3} and piezoelectricity, ability to transform mechanical energy into electrical energy^{4,5}, etc. The best-known industrial applications for this type of material are capacitors, information storage, piezoelectric actuators, infrared sensors and ultrasonic transducers in medical applications and sonar^{6,7}. The PT is also known by a Curie Weiss transition temperature equal to 490°C, a low constant dielectric value of about 200, a spontaneous polarization of about⁸ 80.10⁻⁵ cm⁻² and by a quadracity ratio of about 1.064⁹.

The existence of a structural disorder within perovskite compounds induces drastic changes in the physical properties of these materials. In particular, when making a substitution at the site A or B of the structure, it may in

some cases lead to disordered dipolar compounds exhibiting interesting physical properties in regard to the original multiple industrial applications. In this regard, a great number of works have been devoted to the study and the preparation of the PT ceramics doped with various elements such as zirconium, lanthanum, erbium, calcium or magnesium^{3,9-12}. To our knowledge no publication has been dedicated to the study of Co or Cu doped PT. The present work discussed the effect of the incorporation of Co and Cu elements on the crystal structure of lead titanate ceramics. This incorporation in the PT matrix produces changes in the sites A (and) or B depending on the behavior of the latter during this substitution. With the help of X-Ray Diffraction (XRD) and Raman spectroscopy, we have studied the effect of the dopant concentration in Co and Cu on the structure and Raman modes of Co-doped PT (PCoT_x, 0 ≤ x ≤ 30%) and Cu-doped PT (PCuT_x, 0 ≤ x ≤ 20%).

The results were then analyzed and interpreted. We used the sol-gel method to elaborate these materials due to its advantages, such as low temperature processing, no

*Author for correspondence

vacuum requirement, low cost. The obtained results show that Co has a more pronounced influence than Cu on the structure and the evolution of Raman modes. Indeed XRD has shown that Co induces a transition from the tetragonal to the pseudocubic structure, while addition of Cu does not change significantly the structure.

$\text{Pb}(\text{CH}_3\text{COO})_{2,3}\cdot\text{H}_2\text{O}$, titanium alkoxide $\text{Ti}[\text{OCH}(\text{CH}_3)_{2,4}]_4$, cobalt acetate $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, and copper acetate $\text{Cu}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ as precursors, lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$) as peptizing agent, acetic acid to dissolve the acetates of cobalt. The different steps in the preparation of the $\text{Pb}_{1-x}\text{Co}_x\text{TiO}_3$ (PCoT_x) and $\text{Pb}_{1-x}\text{Cu}_x\text{TiO}_3$ (PCuT_x) powders are illustrated in the flowchart in Figure 1.

2. Procedure

To elaborate the samples we used lead acetate trihydrate

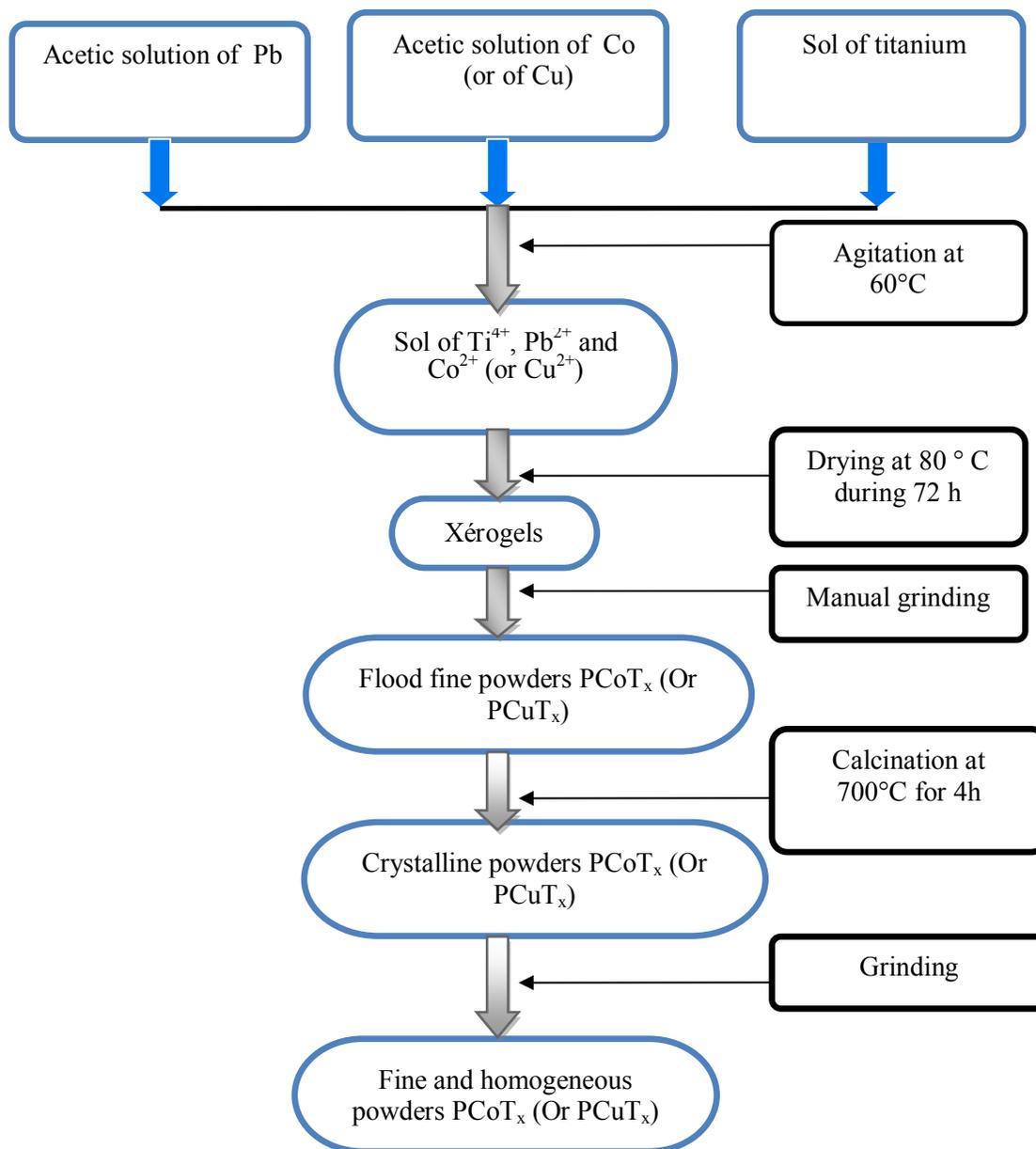


Figure 1. Flowchart of the preparation of the PCoT_x and PCuT_x samples.

3. Results and Discussion

The X-ray diffraction patterns of PCoT_x ceramics ($0 \leq x \leq 30$) are shown in Figure 2(a). These patterns show a pure perovskite structure, without the presence of any secondary phase (pyrochlore). We note that the peaks overlap of 001/100, 101/110 and 201/210, observed in the PT spectrum, disappears completely in the PCoT_x spectra which may be due to the grain size effect and/or local disorder created by the dopant in the PT matrix, and hence an increase of Co concentration induces a decrease of the tetragonality and the structure becomes pseudocubic for x 10%.

Figure 2 (b) shows that the spectra corresponding to the PCuT_x samples, calcined at 700°C for 4 hours, are typical of the perovskite structure. The spectra corresponding to $x=0.1$ and 0.2 show that the two samples crystallize in the tetragonal phase with the presence of secondary phases PbO ($2\theta = 28^\circ$) and CuO ($2\theta = 35^\circ$), the peak corresponding to CuO is slightly more intense for $x = 20\%$, which is apparently due to the solubility limit of copper in PT, and to the fact that the increase in the copper concentration increases the crystallization temperature of the sample in the perovskite phase. Up to 20% in Cu, the ceramic structure remains quadratic as for PT.

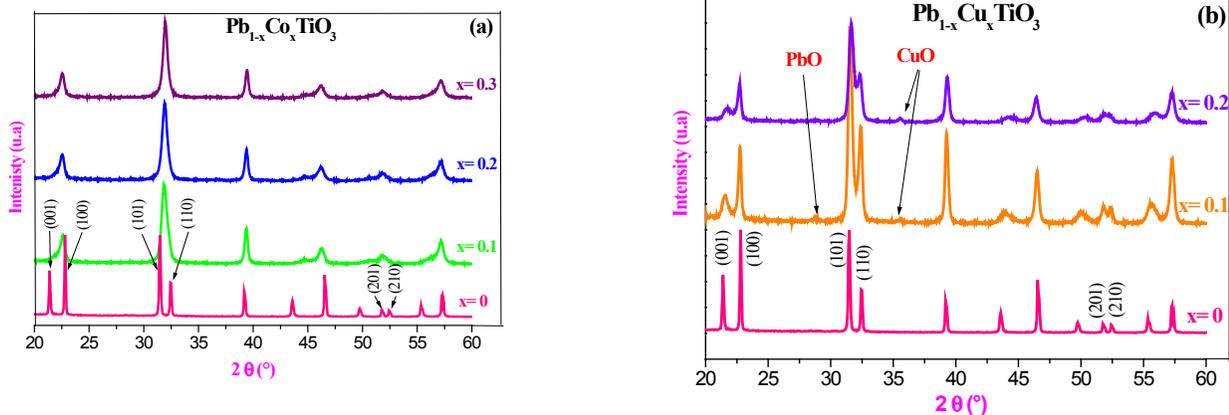


Figure 2. Evolution of the XRD spectra of PCoT_x (a) and PCuT_x (b) samples calcined at 700°C .

Figure 3 shows the variations of the quadracity, c/a , for PCoT_x and PCuT_x , as functions of the dopant concentration. This parameter decreases more rapidly for PCoT_x , especially for $x \leq 10$. The tendency of the structure to transform to the pseudocubic one is more pronounced for PCoT_x .

The room temperature Raman spectra of the pure PT powder and of the various Co and Cu concentrations are

The room temperature Raman spectra of the pure PT powder and of the various Co and Cu concentrations are shown in Figure 4. On the Raman spectrum of the lead titanate ($x = 0$), we observe the presence of ten active phonons modes which is the signature of the presence of the quadratic phase C_4V_6 of $P_m 4_m$ space group confirming the complete crystallization PT in the tetragonal perovskite phase in agreement with the XRD results (Figure 2). In particular are observed a broad and asymmetrical band corresponding to $E(\text{LO}_3)$, a broad intense band at 632 cm^{-1} corresponding to the $A_1(\text{TO}_3)$ phonon mode and the asymmetric broad band near 511 cm^{-1} corresponding to $E(\text{TO}_3)$, a sharp peak at 294 cm^{-1} which is attributed to the B_1 and E modes and a peak near 114 cm^{-1} . With addition of Co ($0 \leq x \leq 30\%$), a decrease in intensity of the modes $A_1(\text{TO}_1)$, $E(\text{TO}_3)$, B_1+E and $E(\text{TO}_2)$ is observed and an expansion of certain bands especially for the sample with $x = 0.3$ (Figure 4 a). For the same dopant concentration, $x = 0.3$, one can also observe a shift to lower frequencies, and the disappearance of the $E(\text{TO}_2)$ and $E(\text{LO}_1)$ modes, indicating the progressive distortion of the tetragonal lattice, and its evolution towards a pseudo-cubic structure. It is possible that, in the case of the pure PbTiO_3 , the PbO and TiO bonds characteristics of the perovskite structure oscillate with different frequencies and, therefore, they

exhibit two different absorption bands B_1+E and $A_1(\text{TO}_2)$. The addition of cobalt seems to couple these two bands located at around 260 cm^{-1} . However in Figure 4(b), we observe a slight decrease in intensity of the modes $A_1(\text{TO}_1)$ and B_1+E and the disappearance of one band $E(\text{TO}_2)$ ($x = 0.1$). The increase of the copper concentration (to $x=0.2$) leads to the disappearance of the second $E(\text{LO}_1)$ mode and the decrease in intensity of other few

modes. This can be explained by pivoting octahedra with non-cubic symmetry.

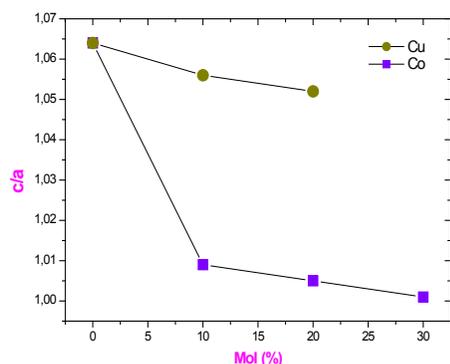
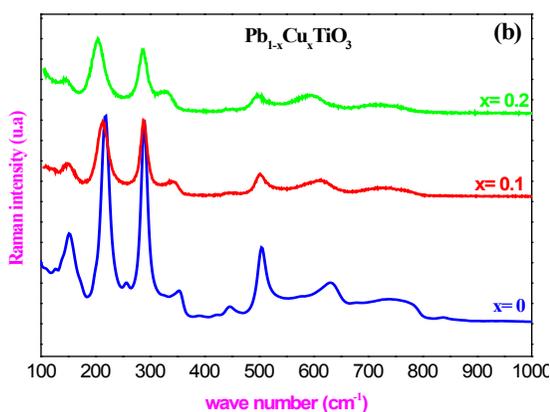


Figure 3. Quadraticity (c/a) variations for PCoT_x and PCuT_x calcined at 700°C .



changes gradually from the quadratic phase towards the pseudocubic one, before its complete disappearance¹³. In addition, the position of both modes decreases with the increase in the cobalt rate, which implies that the cobalt affects all the Raman modes and creates a disorder on the sites concerned with these modes.

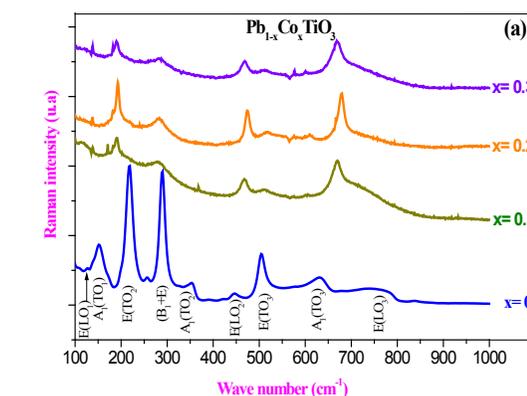
We note on Figure 6 that the frequency of the $\text{E}(\text{TO}_2)$ mode decreases significantly, while the frequency of the $\text{A}_1(\text{TO}_1)$ mode remains almost constant. It is clear then that the $\text{E}(\text{TO}_2)$ mode has been disturbed which confirms the hypothesis of having a disorder in the site A (Pb).

4. Conclusion

The XRD spectra showed that the produced powders, PCoT_x ($0 \leq x \leq 30\%$) and PCuT_x ($0 \leq x \leq 20\%$) are of a good crystalline quality without the presence of any pyrochlore phase.

Figure 4. Raman spectra of PCoT_x (a) and PCuT_x (b) samples calcined at 700°C .

To analyze the influence of the Co and Cu concentrations in PT samples on Raman frequencies and on the Full Width at Half-Maximum (FWHM) we have represented on Figures 5 and 6 the Raman shifts and the FWHM of the two $\text{E}(\text{TO}_2)$ and $\text{A}_1(\text{TO}_1)$ modes for PCoT_x and PCuT_x , as these two modes present a clear signature of the induced change due to the dopant incorporation. Figure 5 shows that the half-value width of the $\text{A}_1(\text{TO}_1)$ mode, representing the vibrations of the cation on the site B, remains constant up to 10% in Co and then decreases with the increase in the cobalt rate. This implies that the site B of the matrix is affected by cobalt when its content is higher than 10%. The $\text{A}_1(\text{TO}_1)$ mode behaves as a soft mode for which the FWHM decreases when the structure of the compound



In fact, the effect of cobalt was observed by the transition from the tetragonal phase to the pseudo-cubic one from above $x = 10\%$. However, samples doped with copper crystallize in the same phase as the pure sample namely the tetragonal phase, but at the expense of the crystallization temperature. The incorporation of a proportion of cobalt or copper in the matrix of lead titanate also has effects on the number, intensity and expansion of certain phonon modes; these effects were shown using the Raman spectra. Moreover, Raman analysis shows that Co occupies both A (Pb) and B (Ti) sites of the ABO_3 (PbTiO_3) perovskite structure of these materials for $x > 10\%$, while Cu occupies the same site A (Pb) in the whole range of concentration.

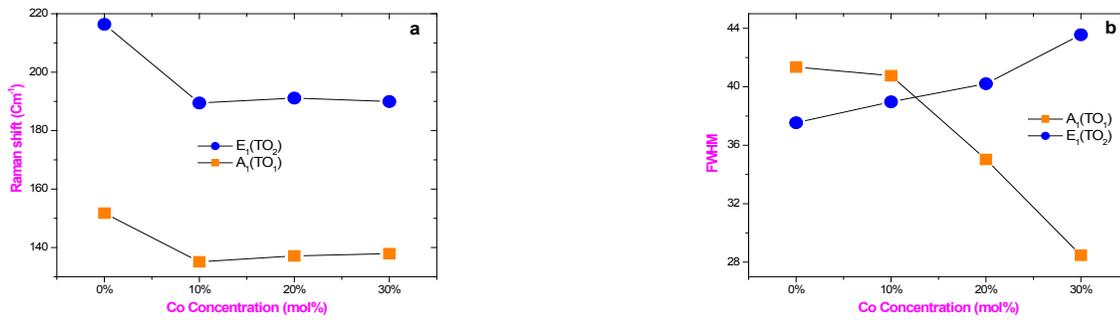


Figure 5. The Raman shift and half-value width of the $E_1(TO_2)$ and $A_1(TO_1)$ modes for $PCoT_x$.

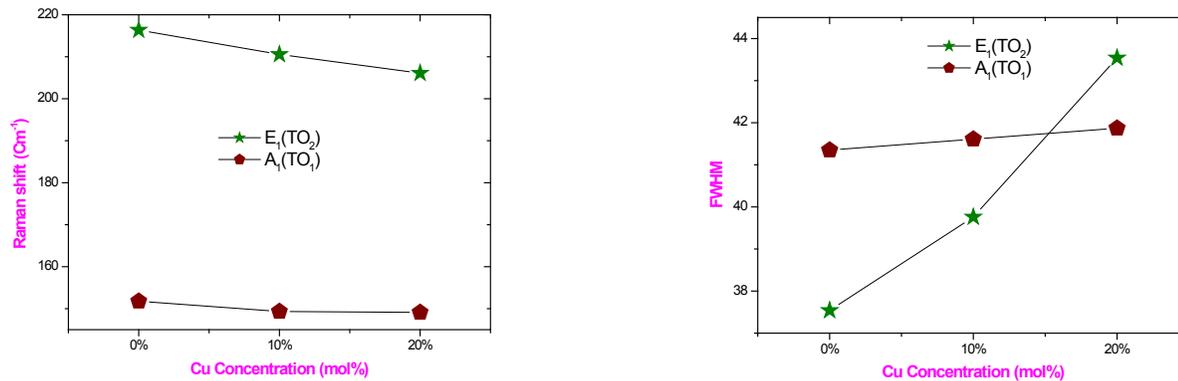


Figure 6. The Raman shift and half-value width of the $E_1(TO_2)$ and $A_1(TO_1)$ modes for $PCuT_x$.

5. References

- Mouna M. Study of a pyroelectric detector nanostructured matrix $Hg(1-x)Cd_xTe/CdTe$ for infrared imaging. Magisterium University of Oran; 2010.
- Guifard B. Preparation and characterization of ceramic ferroelectric PZT type flouré [PhD thesis]. Lyon: National Institute of Applied Sciences; 1999.
- Fadil FZ. Synthesis and characterization of materials PT: LN Mg and Mg/Ho for crystalline fiber manufacture. Cryst Res Technol. (2011); 46:368–72.
- Giraud F. Causal modeling and control of a piezoelectric actuator wave [PhD thesis]. University of Lille I; 2002.
- Bullo M. Modeling and control of the piezoelectric motor wave [PhD thesis]. Lausanne: Faculty of Science and Technology of the Engineer Federal Institute of Technology; 2005.
- Kim S, Jun M-C, Hwang S-C. Preparation of lead titanate ceramics undoped via sol-gel processing. J Am Ceram Soc. 1999; 82:289.
- Yakovlev S, Solterbeck C-H, Es-Souni M, Zaporojtchenko V. Rare-earth ions doping effects on the optical properties of sol-gel fabricated $PbTiO_3$ thin films. Thin Sol Films. (2004); 446:50–3.
- Kellati M. Preparation by the sol-gel ceramic materials and characterization of lanthanum doped perovskite $PbTiO_3$ ($Pb_{1-x}La_xTi_{x/4}$) [PhD thesis]. Faculty of Sciences Dhar El Mehrzaz Fez; 2002.
- Elmesbahi A, Elaboration by the sol-gel process and physicochemical study and dielectric of $PbTiO_3$ calcium-doped and the lanthanum [PhD thesis]. Ph.D at the FSDM Fez Morocco; 2006.
- Mrharrab L. Study of the physicochemical properties of $PbZr_xTi_{1-x}O_3$ ($0 \leq x \leq 0.91$) and $PbTiO_3$ pure and doped (V, Cu, Bi, Mn, Mg, La, Ca) prepared by solid route [PhD thesis]. FSDM Fez; 2014.
- Bouayad K. Elaboration by sol-gel and characterization of ferroelectric ceramics structure perovskite lead zirconate titanate doped lanthanum [PhD Thesis]. FSDM Fez Morocco; 2005.

12. Paris EC, Gurgel MFC, Boschi TM, Joya MR, Pizani PS, Souza AG, Leite ER, Varela JA, Longo E. Investigation on the structural properties in Er-doped PbTiO_3 compounds: A correlation between experimental and theoretical. *J Alloys Comp.* 2008; 462:157.
13. Dobal PS, Majumder SB, Naskar SB, Katiyar RS. Microraman probing of short-range disorder in lanthanum-doped lead titanate films. *J Raman Spectrosc.* 1999; 30:567.