SYNTHESIS AND CHARACTERIZATION OF LEAD OXIHYDROXYCARBONATETHIN FILMS

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In this work we studied a new material thin film basedin a modification for lead sulfide thin films formulation. The characterizations were: optical microscopy of the surface, where can be observed certain homogeneity at large scale, surface morphology by Scanning Electron Microscopy, here we could to observe clusters of circulars and fibers shapes; surface profilometry was used to measure the film thickness giving a value of 13.67μm. Top and perspective views of Atomic Force Microscopy reveal us the formation of fibrillated aggregates, X-rays Photoelectrons Spectrum show to us the chemical composition of the material thin film, with this analysis we could to observe the cleanness of the chemical bath deposition technique, because only were present lead, oxygen and the carbon elements, those that are hoped. Finally we determine the energy band gap from the absorption, with the value of 3.32 eV.

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1. Introduction

The chemical bath deposition (CBD) is an inexpensive and low temperature method (25-90°C) that allows depositing large area semiconductor thin films[1-3]. It is based on the controlled precipitation of the material to be prepared, so that produces a film upon the substrate surface. Precipitation can be controlled by adjusting the experimental conditions (chemical composition, pH, reaction time and process temperature, among others)[4-6]. Chemical bath deposition method has fundamental advantages over other techniques, such as the use of relatively low temperatures, cheap instruments, convenience in handling, and easiness in composition control, making it very useful for the large scale and environmentally benign synthesis of materials[7,8]. If we prepare a film of hydroxide or oxide-hydroxide by an ion-by-ion deposition process andsubsequentlywe heat it in a controlled oxygen atmosphere, dissociation takes place, resulting in a pure oxide film[9,10]. Metal-Oxide thin films currently find applications in various fields such as sensors, catalysis and electronics, making them essential in modern human society[11,12].

Thin films of lead oxyhydroxicarbonate have been properly deposited on to glass slides using chemical bath deposition. The films generally show a high transmittance (60-80%) in the Vis-NIR regions of the electromagnetic spectrum. The absorbance is of the order of 85% near the UV region and decreases with longer wavelength. The band gaps of the oxide films are in the

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range of 2.90-2.95 eV,also oxides have values of refraction index greater than 2.0 in this spectral range[13].

In this paper are made reproducibility studies of a new route for the synthesis of lead oxyhidroxicarbonate thin films, $Pb_{10}O(OH)_6(CO3)_6$, using the CBD technique. The optical properties, the structural and morphological characterization and the chemical composition of the thin films were presented.

2. Experimental procedures

The used technique to grow our material layer of lead oxyhidroxicarbonate was the chemical bath deposition; we start from a formulation to growPbS thin films with triethanolamine,but suppressing the thiourea. For the synthesis of the material, firstly a solution A was prepared, which contained: water, ammonium hydroxide and rongalite. Thereafter, the solution was heated to reach a temperature in the range of 80 to 90°C. In addition, the substrates were cleaned with soap and were rinsed with distilled water after that were dried.

The main reaction was prepared by adding 5ml of lead acetate at 0.5M, 5 ml of sodium hydroxide at 2.0M, 2ml of triethanolamine at 1.0M,82ml of distilled water and 6ml of solution A. It is important to add the compounds in the sequence established and then introduce the substrates vertically in the chemical mixture.The complete solution was heated to reach 75°C, after that thermal bath was turned off to reach room temperature.Two hours after starting the substrate is removed and cleaned with distilled water without scrubbingand deposited again. 24 hours after starting the coated substrate is removed and washed thoroughly rubbed with cotton and distilled water, then allowed to dry. It is recommended that the reaction must be realized in darkness conditions, because this one is sensitive to the light.

The X-ray diffraction measurements were performed using a Bruker D8 Advance X-Ray Diffractometer. Optical transmission spectra were recorded by a Perkin-Elmer, model Lambda-19 UV/VIS/NIR spectrometer in the 280-850 nm wavelength range. The morphology of the samples surface was obtained by Atomic force microscopy (AFM) using a JSPM-4210 scanning probe microscope (JEOL Ltd). Chemical composition was done in a Perkin-Elmer PHI 5100 XPS, the Raman dispersion was carried out Micro ramanX'Plora BXT40 con resolution de 2400T and the scanning electron microscopy image was obtained by XL30-ESEM Scanning Electron Microscope.

3. Results and discussion

The Fig. 1, we can see the optical responses of absorption and transmission of the material that we are studying, here it can observe that the transmission is very low between 200 and 300nm, from here it begins to increase in a very abrupt way, until reach a value close to 50% in 380nm. The transmittance remains in the range of 50 to 70% between the 380 and 800nm, this can be interpreted as opacity of the film.

The inset of Figure 1 it is shows the geometric basis for calculation of the energy bandgap of the produced material. It can be observed that have taken the direct transitions as the base and the first ramp is considered as background, the next slope was used for the linear fit which was used to calculate the bandgap value of 3.32 eV.

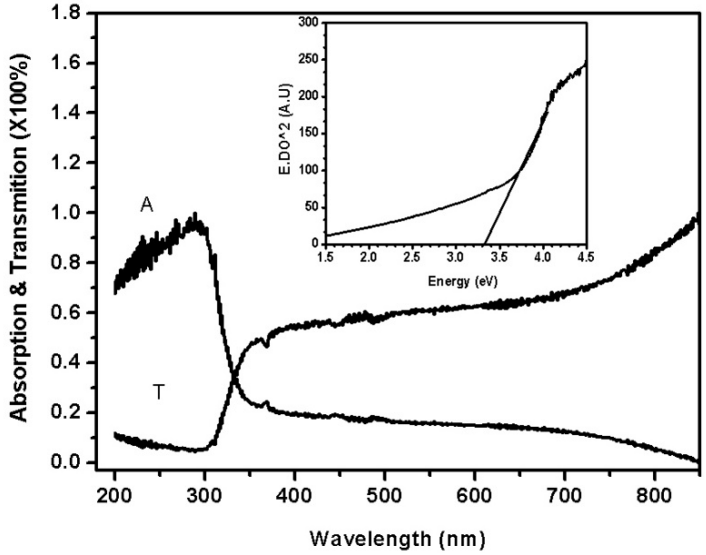

Fig. 1. Spectra of absorption, transmission of Lead oxyhidroxicarbonate, and inset for calculate the bandgap.

In Figure 2 there appears therelief profile of the Lead oxihidroxicarbonate orethin films, elaborated with the previous described condition. From here we obtained the thickness considering a level of reference placed in 4071.36 µm of the sweep in which the height of the top is of 136.708 k Å and the second level of reference placed in 7380.67µm with a height of the top of 8 Å. This gave to us a measurement of thickness of 13.67µm.

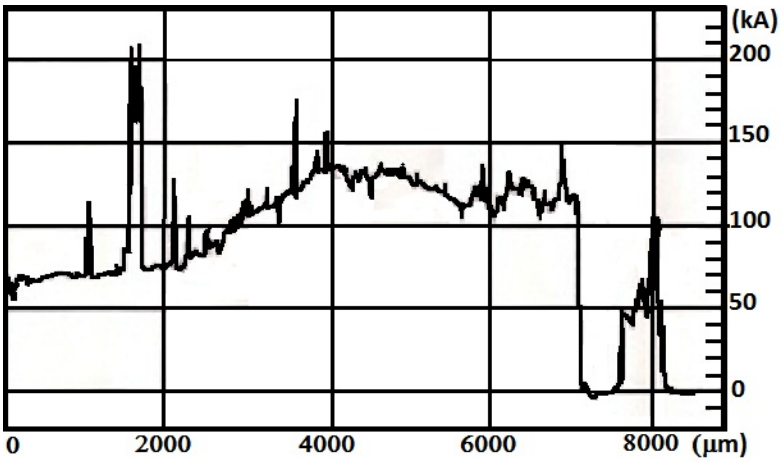

Fig 2. Plot of the cross section profile of the Lead Oxyhydroxicarbonate film.

At Figure 3 the superficial morphology of Lead Oxyhydroxicarbonate ore, obtained by an Optical Microscope is depictedusing a magnification scale of 100 X. Here we can observe cluster distributions which protrude from flatness.

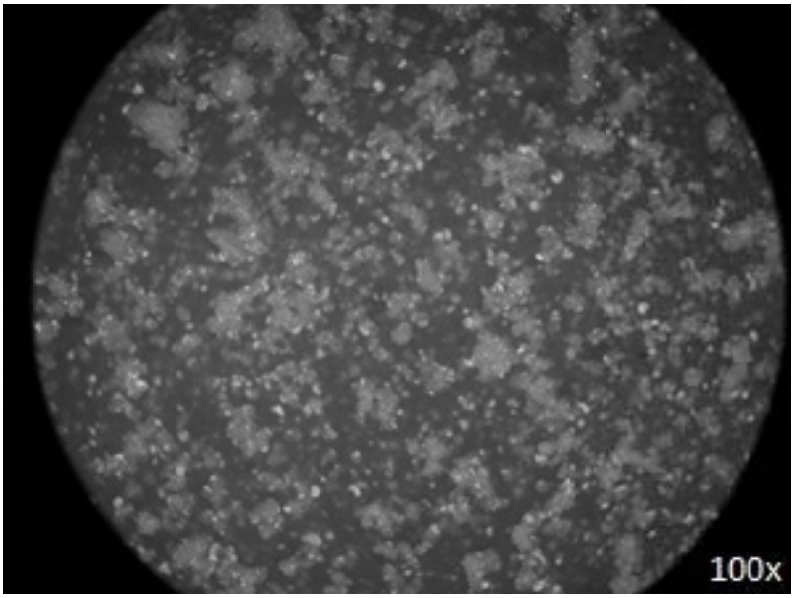

Fig. 3. Optical image of the surface, the scale as indicated.

Fig. 4 presents the distribution of wafers of the material with a background covered by entangled fibers. The chemical composition of all this shapes are de same.

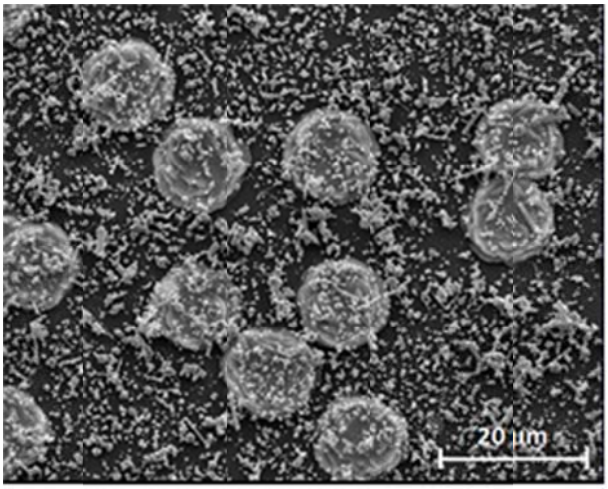

Fig. 4.SEM image of the surface of the Lead Oxyhydroxicarbonate film.

In Figure 5 the superficial morphology of lead oxihidroxicarbonate ore was obtained by a Microscope of Atomic Forcein tapping mode, the bottom part of figure (a), is a frontal sight in which it appreciates the formation of fibers for this material, the level differences are of 1.52 µm and in the upper part presents a perspective sight in the sector where the sample considered has a maximum level difference of 1.2 µm and the roughness average obtainedwith the software was 0.14µm[14]. These formations extended uniformly must be considered as clusters of material grains.

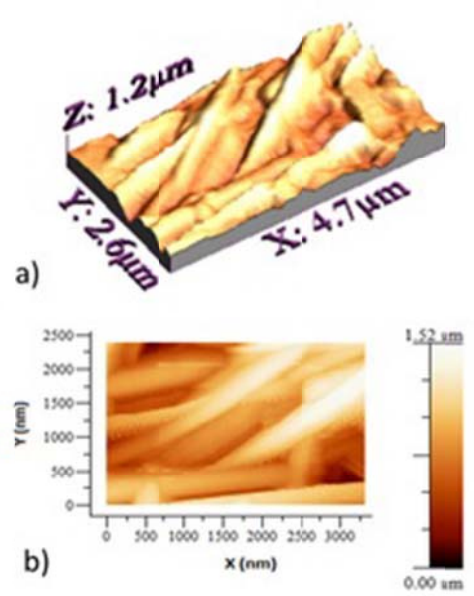

Fig. 5.Micrography AFM that shows the superficial morphology of the studied films. a) a frontal sight. b) a sight in perspective.

The chemical composition that shows the XPS spectrum revealed that the obtained materials by chemical bath have a selective purity without excessive pollutants. The expected elements were those obtained. In figure 6 can be appreciated the present elements, Pb, O and C, in our material layer, as are indicated by labels.In Table 1 are the atomic percent values of the present elements in our material layer.

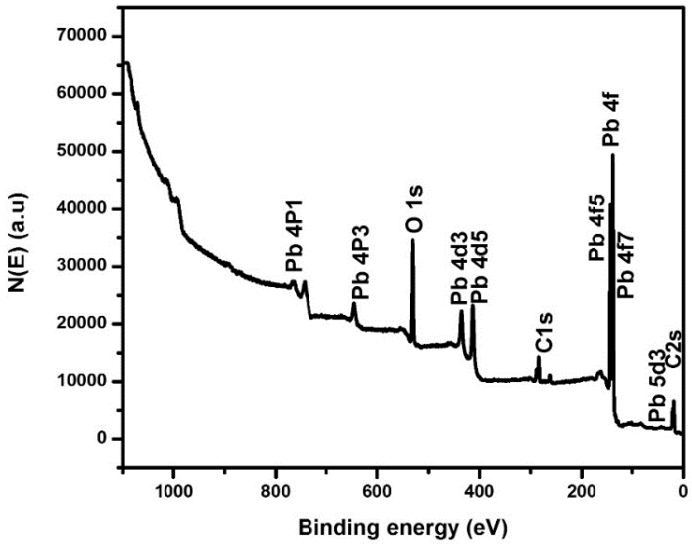

Fig. 6. XPS spectrum of lead oxihidroxicarbonate from 0 to 1100 eV range.

Table 1. Atomic percent values of the present elements in our material layer.

Atomic Concentration	Elements
19.6 %	Pb 4p1
6.5 %	Pb 4p3
31.0 %	O1s
6.9 %	Pb4d3
5.7 %	Pb4d5
8.4 %	C1s
11.8 %	Pb4f
10.1 %	C2s

Typically the lattice vibrations appear from 10 to 200cm^{-1} region and the metallic with oxygen atom interaction are presented at the 200 to 450cm^{-1} region[15]. The characteristic vibrational micro Raman modes for lead oxihidroxicarbonate are depict in the Figure 7 for a wave vector region 100-4000 cm^{-1}, while micro Raman vibrational bands of carbonates are shown at 1050, 1053 and 1056 cm^{-1}, see the inset of Figure 7 and corresponding to three different occupied sites of the carbonate (CO_3^-) ions in the crystalline cell. At the same time, Figure 7 shows a micro Raman spectrum, where depict a stretching band of the hydroxyl group placed at 3639 and 3571cm^{-1}. The mean band peaks deconvoluted with two Gaussian functions showing the same number of Raman peaks of the different sites in the crystalline cell of the stretching (OH) groups. Similar procedure of deconvolution was performed with three peaks of the carbonate bands.

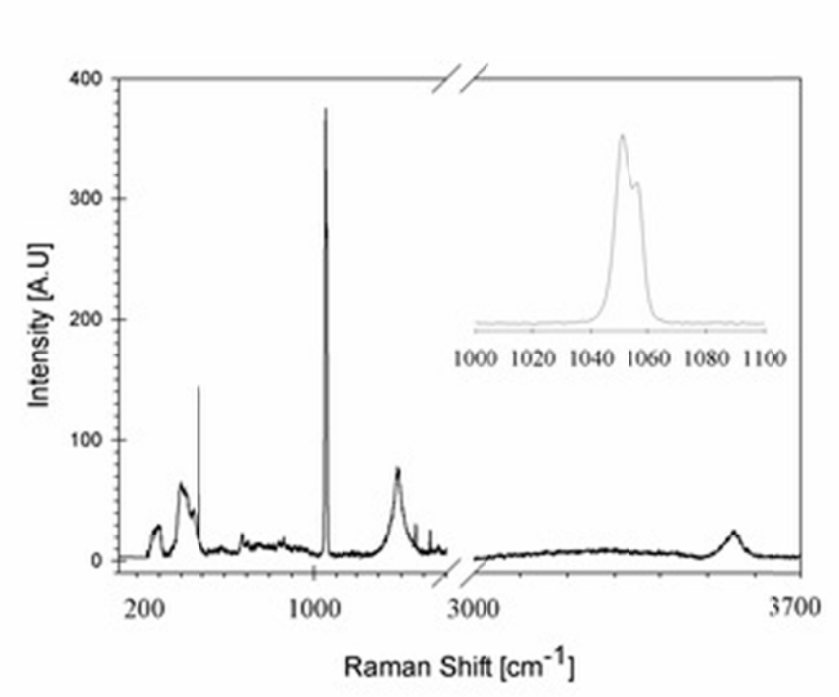

Fig. 7. Raman spectrum of lead oxihidroxicarbonate in the 100-3700cm^{-1} range.

The Figure 8 one presents the spectrum of diffraction of X-rays of the Lead oxihidroxicarbonate, since it is possible to observe the films that were elaborated they are polycrystalline and agree with the material that is indicated comparing with the database PDF *19-0680. This Spectrum of Diffraction was obtained of the residual powders that they precipitate in the glasses of reaction where the films are large.

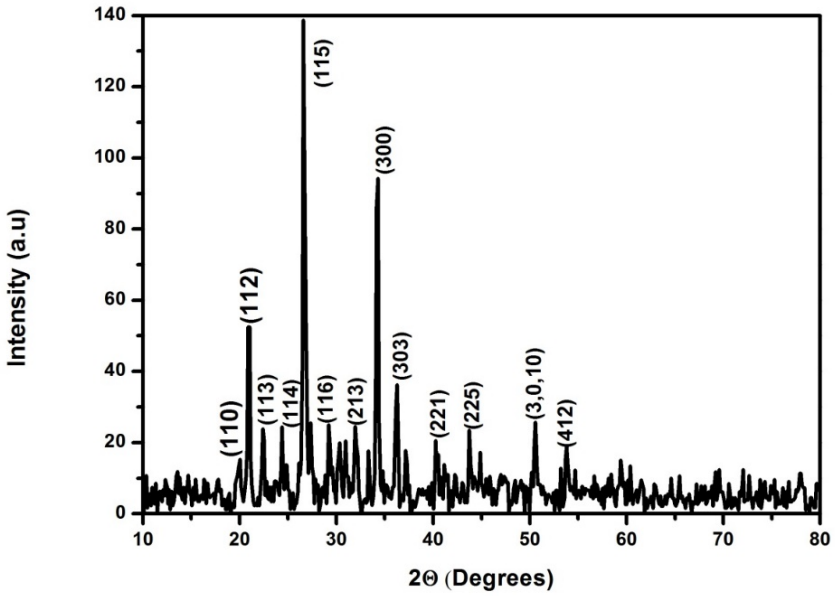

Fig. 8.Diffraction of X-rays of the oxihidroxicarbonate of lead $Pb_{10}O(OH)_6(CO_3)_6$

4. Conclusions

In this work the morphological optical, chemical and structural features of the lead oxyhidroxicarbonate films were presented. Also, there were made reproducibility studies of a new route for the synthesis of material using the CBD technique, this material ore is denominated as *plumbonacrite* in the literature. The films obtained present a direct band gap of 3.32 eV with a semitransparent optical characteristics. The films shows a average roughness of 0.14 μm and thickness of 13.46 μm.

The films that were elaborated are polycrystalline with a preferential orientation of (1,1,5) with a hexagonal structure. Finally the Raman results presented all the different vibrational modes associated to the CO_3, OH ions and Pb-O bonds which is a proof of the stoichiometric combination.

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