Materials Research Bulletin 49 (2014) 172–175

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Nanostructured hydrocerussite compound ($Pb_3(CO_3)_2(OH)_2$) prepared by laser ablation technique in liquid environment

D.L. da Cunha [a,*], G.F.C. Pereira [b], J.F. Felix [c], J. Albino Aguiar [a,b], W.M. de Azevedo [a,d]

[a] *Programa de Pós Graduação em Ciência de Materiais, Universidade Federal de Pernambuco, Avenida Prof. Moraes Rego, 1235, Cidade Universitária, Recife, PE, 50670-901, Brazil*
[b] *Departamento de Física, Universidade Federal de Pernambuco, Avenida Prof. Moraes Rego, 1235, Cidade Universitária, Recife, PE, 50670-901, Brazil*
[c] *Departamento de Física Universidade Federal de Viçosa. Av. P H Rolfs, s/n, Campus Universitário, Viçosa, MG, 36570-000, Brazil*
[d] *Departamento de Química Fundamental, Universidade Federal de Pernambuco, Avenida Prof. Moraes Rego, 1235, Cidade Universitária, Recife, PE, 50670-901, Brazil*

ARTICLE INFO

Article history:
Received 10 March 2013
Received in revised form 30 June 2013
Accepted 18 August 2013
Available online 4 September 2013

Keywords:
A. Inorganic compound
A. Nanostructures
B. Chemical synthesis
C. X-ray diffraction
D. Microstructure

ABSTRACT

This article presents a chemical bottom-up synthesis of highly crystalline and nanostructured hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) with hexagonal morphology prepared by laser ablation in liquid. The results demonstrate that is possible to use laser ablation in liquid to prepare complex chemical compounds. The experiment consisted of a high power second harmonic of an Nd:YAG laser incidence on the surface of a Pb target immersed in primary alcohols. Three different values of fluency and four different primary alcohols were used in order to investigate the influence of fluency delivered to the target surface and the chemical composition of the liquid environment on the properties of the prepared materials. Crystalline and nanostructured hexagonal particles of hydrocerussite, with average widths of 1.0 ± 0.3 μm and average thickness of 80 ± 20 nm, were obtained when laser ablation was done in methanol and ethanol whereas hydrocerussite and metallic lead were obtained when 1-propanol or 1-butanol were used. Additionally, it was shown that the values of the laser fluency used in this study do not modify the sample morphology and composition. In order to explain the observed results a photochemical reaction model induced by laser ablation of a metallic Pb surface immersed in alcohol solution is presented.

1. Introduction

Laser ablation of solid targets in liquid medium has been extensively used in the past two decades, at the beginning as a technique to produce a colloidal solution of nanoparticles, and subsequently as a successful material fabrication technique that is able to quickly prepare nanostructured materials of various compositions, morphologies and phases [1,2]. The reason for that choice seems to be the fact that laser ablation in liquid can be considered as a chemically clean and a one-pot synthetic route that are able to prepare a variety of functionalized new nanostructures, where the final product is usually obtained without by-products and no need for further purification. Also it is a low cost experimental technique, which presents few controlled parameters and provides extreme confined conditions of high temperature and pressure that favor the formation of unusual metastable phases. However, over the majority of laser ablation results found in the literature, it can be observed that this methodology has been used to obtain materials such as: metal oxides, metal colloids, semiconductor, and nitrites [3–10]. Few examples of more complex compounds obtained by laser ablation can be found in the literature: it was developed a catalyst free electrochemistry-assisted pulsed laser ablation in liquid route to fabricate polyoxometalate nanostructures $Cu_3(OH)_2(MoO_4)_2$ [11]; also it was presented a surfactant-assisted preparation method to obtain layered silver bromide-based inorganic/organic nanosheets by pulsed laser ablation in aqueous media [12]. Additionally, the size and morphology of nanoparticles has been modified [13,14] by adjusting the variables that control the composition and the structure of nanomaterials generated by laser ablation in liquid environment [15].

Aiming to contribute to the development of this area, we present a chemical bottom up synthesis of nanostructured and highly crystalline hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) compound with hexagonal morphology, prepared exclusively by laser ablation technique in a liquid environment.

Hydrocerussite $Pb_3(CO_3)_2(OH)_2$ is quite a rare mineral in nature that is found in small quantities in soil only. It consists of basic lead carbonate with a trigonal crystalline structure. Its hexagonal atomic layers overlap along the direction (0 0 1) which promotes

* Corresponding author. Tel.: +55 81 9755 2072; fax: +55 81 2126 8442.
E-mail addresses: diegolcunha@gmail.com (D.L. da Cunha), gp91@df.ufpe.br (G.F.C. Pereira), jorlandiof@gmail.com (J.F. Felix), albino@df.ufpe.br (J. Albino Aguiar), wma@ufpe.br (W.M. de Azevedo).

0025-5408/$ – see front matter
http://dx.doi.org/10.1016/j.materresbull.2013.08.030

the growth of hexagonal structures, where layer A consists of Pb and CO_3, and layer B of Pb and OH, with a stacking sequence of the type BAABAA [16]. Although hydrocerussite is rare in nature and it has been playing a significant role in geology and in environmental issues [17], it has also been applied as a polymer stabilizer [18] and it has been extensively investigated in the lead acid battery industry [19]. The literature shows that experimental crystallization and thermodynamic data on Pb carbonates are limited, and the characterization of these properties requires an adequate amount of samples but unfortunately the mineral is rare and never occurs in a sizeable amount. Regarding to the synthesis of hydrocerussite, most methods found in the literature are awkward and time consuming [20,21]. To overcome these difficulties and to present an example of more complex inorganic compound synthesis using laser ablation technique, we present in this paper the laser ablation technique in the liquid environment as a straightforward synthetic route for the preparation of nanostructured hydrocerussite $Pb_3(CO_3)_2(OH)_2$ compound.

2. Experimental

Fig. 1 shows the experimental scheme used to synthesize the nanostructured Pb carbonate compound, where a metal plate of Pb (99.5%, America Elements) used as target material was placed on the bottom of a glass vessel filled up with 10 cm^3 of alcohol solution. The target was irradiated for 10 min with the second harmonic of a pulsed Nd:YAG laser (Spectra-Physics Quanta-Ray GCR-170) operating at 532 nm and 10 Hz, with 8 ns of pulse width, which was focused on the target with a spot size of about 1 mm in diameter using a 100 mm focal length lens.

Finally, the products were centrifuged and collected. The solutions obtained including sediments were dropped and dried on glass substrates for sample characterization. For comparison of the results, three different laser fluencies on the solid target were used 0.5 J/cm^2, 2.0 J/cm^2 and 4.0 J/cm^2, and in order to establish the mechanism for preparing the sample, the ablation reaction was performed in methanol (Merck PA), ethanol (Kinetics PA), 1-propanol (Merck PA) and 1-butanol (Merck PA), for which the experimental setup is summarized in Table 1.

The morphology of the samples was analyzed by scanning electron microscope using a Jeol microscope model JSM-5900, where the samples were previously metalized with 10 nm of Au thin film by sputtering, model SC-701 Quick Coater form Sanyu Electron. The UV–vis spectra where recorded using an Ocean Optics CHEM2000-UV-VIS spectrometer, whereas the crystal structure and the infrared analysis were obtained using Siemens X-ray diffraction analyze model D5000 with Cu $K\alpha$ radiation and a Bruker FTIR spectroscope model IFS 66, respectively.

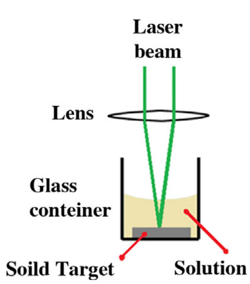

Fig. 1. Schematic diagram of the experimental setup for nanoparticle production.

Table 1
Experimental parameters used for the laser ablation of the Pb target in this work.

Sample Name	Solid Target	Liquid Environment	Liquid Volume	Fluency	Repetition Rate	Ablation Time
PbMet-A	Pb Plate	Methanol	10 cm^3	2.0 J/cm^2	10 Hz	10 min
PbMet-B	Pb Plate	Methanol	10 cm^3	0.5 J/cm^2	10 Hz	10 min
PbMet-C	Pb Plate	Methanol	10 cm^3	4.0 J/cm^2	10 Hz	10 min
PbEtha	Pb Plate	Ethanol	10 cm^3	2.0 J/cm^2	10 Hz	10 min
PbPro	Pb Plate	1-Propanol	10 cm^3	2.0 J/cm^2	10 Hz	10 min
PbBut	Pb Plate	1-Butanol	10 cm^3	2.0 J/cm^2	10 Hz	10 min

3. Results and discussions

It is already known that the ablation of a surface of a solid target immersed in a liquid environment causes the ejection of a plasma plume containing atomic neutral and ionized specimens of both liquid and ablated solid [1,2]. Inside the plasma plume, heated by the laser beam and confined by the liquid environment, the pressures and temperatures reach values of about 10^6 Pa and 10^3 K [22]. These critical conditions added to the rapid cooling caused by the liquid environment favors the occurrence of chemical processes in non-equilibrium conditions and the formation of materials with metastable configurations [23]. Using this non-conventional synthetic route, the ablation of the Pb target produces Pb atoms, ions and Pb particles that became dispersed in the liquid environment and subsequently interacted with adsorbed O_2 to form the lead oxide, PbO. This statement can be confirmed by the result presented in Fig. 2 that shows the UV–vis spectra of the irradiated solutions taken immediately after the ablation process. The spectra of all samples shows two absorption bands around 210 and 250 nm which can be assigned to Pb and PbO nanoparticles absorption bands [24,25]. During the experiment this rich environment of ions and particles assisted by the laser radiation may behave as a catalyst surface for the oxidation of the alcohol molecule resulting in a complete decomposition of methanol into CO_2 and H_2O, which subsequently reacts with PbO resulting in the hydrocerussite compound. The synthesis may occur according to the scheme below:

$$Pb_{(solid)} + h\nu + O_2 \rightarrow nPb + Pb^{+m} + PbO$$

$$h\nu + nPb^0 \text{catalyst}$$

$$CH_3OH + O_2 \rightarrow CO_2 + H_2 + H_2O$$

$$3PbO + CO_2 + H_2 \rightarrow Pb_3(CO_3)(OH)_2$$

This assumption is supported by the experimental results already published in the literature on the photochemistry of methanol [26], the decomposition of methanol on metallic surfaces [27] and the results of photo decomposition of alcohols with metal ions in solution induced by radiation [28].

A few hours after the ablation procedure finished a whitish powder precipitate was obtained when methanol and ethanol were used as liquid environments, while a grayish color solution was obtained when 1-propanol or 1-butanol was used. In order to

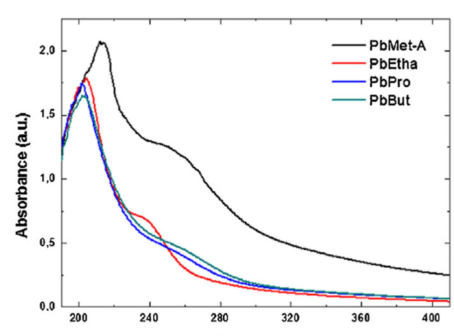

Fig. 2. Pb and PbO absorption bands on the UV–vis spectra of the irradiated solutions.