SYNTHESIS AND CHARACTERIZATION OF $CaTiO_3Pr$ FILMS

CONSTANTIN GHEORGHIES[1], ONUT VALERIU ATANASIU[2],
ALINA-MIHAELA CANTARAGIU[2], LIVIA GHEORGHIES[3]
[1]*"Dunarea de Jos" University of Galati, Faculty of Sciences, 800201, Galati, Romania,*
[2]*"Dunarea de Jos" University of Galati, Department of Physics, Doctoral School, 800201, Galati, Romania*
[3]*"Dunarea de Jos" University of Galati, Faculty of Material Science and Metallurgy, 800201, Galati, Romania*

Abstract. *This study related on the synthesis and characterization of coatings consisting of $CaTiO_3Pr$ by sol-gel and electrochemical deposition techniques in different working conditions. An electrolytic bath containing salts of Ca, Ti and Pr, respectively and methyl alcohol has been used in order to prepare $CaTiO_3Pr$ coatings over copper substrates. The surface morphology observed by means of scanning electron microscopy technique (SEM) showed various shapes crystallites onto copper substrates specified to $CaTiO_3Pr$ complex. The structural analyses are carrying out by means of X-ray diffractometry (XRD) method. The XRD results reveal a mixture of crystalline phases of TiO_2 and Pr particles due to the increasing of orientation degree of crystallites on specific crystallographic directions.*

Keywords*: $CaTiO_3Pr$, sol-gel technique, electrochemical deposition, chrono-amperometrical method, structure.*

1. INTRODUCTION

Phosphorescent materials are more and more present in every day's life. apart from traditional and historical applications in lighting, screens, solid state lasers, optical communication, optoelectronics or sensors, this subject continues to have a major technological role in the fields such as marine and aeronautical navigation [1, 2], nuclear medicine [3], archaeology [4], environment [5, 6], energetic [7], and also organic and inorganic light emitters such as plasma displays, lcd displays, and oled displays, bioinformatics, biophysics, biochemistry, quantum chemistry etc. [8, 9].

At room temperature, the structure of the $CaTiO_3$ mineral is orthorhombic and is made up of corner shared TiO_6 octahedral with Ca ions in the large cavities at the corners of the unit cell. The praseodymium ions (Pr^{3+}) are expected to occupy the Ca sites [10]. This situation results in the presence of two very short Pr^{3+} - Ti^{4+} inter-atomic distances of 3.17 Å, which makes possible a photon assisted energy transfer from Pr^{3+} to Ti^{4+} at relatively low energy. This energy transfer, referred to as $Pr^{3+}/Ti^{4+} \leftrightarrow Pr^{4+}/Ti^{3+}$ Inter Valence Charge Transfer (IVCT) has been proved to interfere strongly with the excited dynamics of the Pr^{3+} ion in $CaTiO_3Pr^{3+}$.

The goal of this paper was the obtaining and characterization of $CaTiO_3Pr^{3+}$ films by means of sol-gel and electrodeposition techniques. Copper with circular geometrical shaped was chosen like as substrate for electrodeposition technique. The chrono-amperometrical method was used for coating during 10 min deposition time at 30 ºC. The surface morphology and crystalline structure were analyzed by means of scanning electron microscopy and X-ray diffractometry techniques, respectively. The obtained results from the two obtaining method were compared and discussed.

2. EXPERIMENTAL

$CaTiO_3Pr^{3+}$ is an exceptional compound regarding to its applicability in a number of different technological fields. This phosphor is a very promising material for low voltage field emission display [11].

2.1. SOL-GEL METHOD DEPOSITION TO PREPARE THE COMPOUNDS

The sol-gel technology is a very powerful method to prepare the inorganic polycrystalline compounds with controlled grain sizes, morphologies and textures in the micro- or nano-meter scale in different working conditions (Fig. 1). Also this technology is very useful for films coating deposition whereas the other methods were used to obtain the $CaTiO_3Pr$ compounds by spin coating, dip coating, radio-frequency sputtering or spray pyrolysis techniques.

2.2. ELECTROCHEMICAL METHOD DEPOSITION TO PREPARE THE COMPOUNDS

An advantageous production method to prepare inorganic polycrystalline compounds is the electrodeposition process from an electrolyte solution containing Pr dispersed metallic particles. By using this technique, the $CaTiO_3Pr$ coatings with controlled morphologies, textures and grain sizes were obtained. However, the amount and distribution of Pr^{3+} particles incorporated during the electrochemical deposition depend on a variety of working parameters: current density, temperature, stirring and deposition time.

Composite coatings consisting of Pr particles in a $CaTiO_3$ matrix have been electrodeposited onto copper substrates (active area 0.196 cm^2) from an electrolyte solution which contains $PrCl_3$ heptahydrate, $CaCl_2$ dihydrate and $TiCl_4$ solution diluted in 50 ml methanol with a pH of 1.7 at room temperature. Two depositions were carried out in different conditions, first at 0 °C temperature with deposition time of 130 min and the second at 30 °C temperature during 130 min deposition time. The temperature was controlled with a thermostat (model VEB MLW Prufgerate-Werk Medingen/Sitz Freital).

A three electrode system with a cell volume of 100 ml was used to perform the experiments. The anode was a platinum wire (electrode area 0.01 dm^2) and a saturated electrode of Ag/AgCl was used as the reference electrode. The surface copper substrates such as the cathode were prepared by mechanical polishing with fine grained emery paper (300, 600 and 800), degreased in acetone and ethanol for a few seconds, washed with doubly-distilled water and dried with warm air. Before and after deposition the samples mass was measured using an electronic balance (model ESJ200-4). A decreasing of mass by a 10^{-4} order can be noted. The electrochemical coatings were carried out by means of chrono-amperometry method with a potentiostat/galvanostat VoltaLab10 interfaced with VoltaMaster4 software for data acquisition and analysis. The plating solution was mechanically stirred (500 rpm) using a rotating disc electrode (model EDI101) with an accuracy of ±2 rpm (revolution per minute) and controlled by CTV101 speed control unit to adjust and control the rotation speed. After the deposition, the samples were rinsed with distilled water to remove loosely adherent particles. The electrical conductivity of the electrolyte solution was recorded by means of a Consort C931 device.

2.3. SURFACE MORPHOLOGICAL CHARACTERIZATION OF SAMPLES

The surface morphology of samples were examined by means of scanning electron microscopy (SEM) using a Quanta 200 Philips FEI device. The inorganic composite surfaces are analyzed at SEM in secondary electron regime.

2.4. STRUCTURAL CHARACTERIZATION OF SAMPLES

The crystallographic characteristics of the samples were analysed through the X-ray diffraction method (XRD) using DRON-3M diffractometer. XRD spectra were recorded at room temperature, the diffractometer using CuK_α radiation in 2θ configuration ranged between 20° and 50°, at 40 kV tension and 30 mA current intensity with a scanning speed of 0.02^o min^{-1} and acquisition time of 0.1 s/step.

3. RESULTS AND DISCUSSION

3.1. SYNTHESIS AND CHARACTERIZATION OF DEPOSITS BY SOL-GEL TECHNIQUES

Sol-gel deposition was accomplished by immersion and after a thermal treatment in the atmosphere. The $PrCl_3$ heptahydrate and Ca and Ti salts were chosen like as precursors and interact to form the sol and silica was used like as substrate. Fig. 1 indicates the morphology of the $CaTiO_3Pr$ film obtained by sol-gel technique. At low temperature the film has an amorphous and porous structure [10]. The higher the temperature, the more defined the crystallographic layout will be. The film features are influenced by the chemical composition of the solution, the deposition parameters as well as those during the thermal treatment (time, temperature and cooling conditions). A highly homogeneous coating and complex crystallites with various sizes and geometrical shapes can be seen.

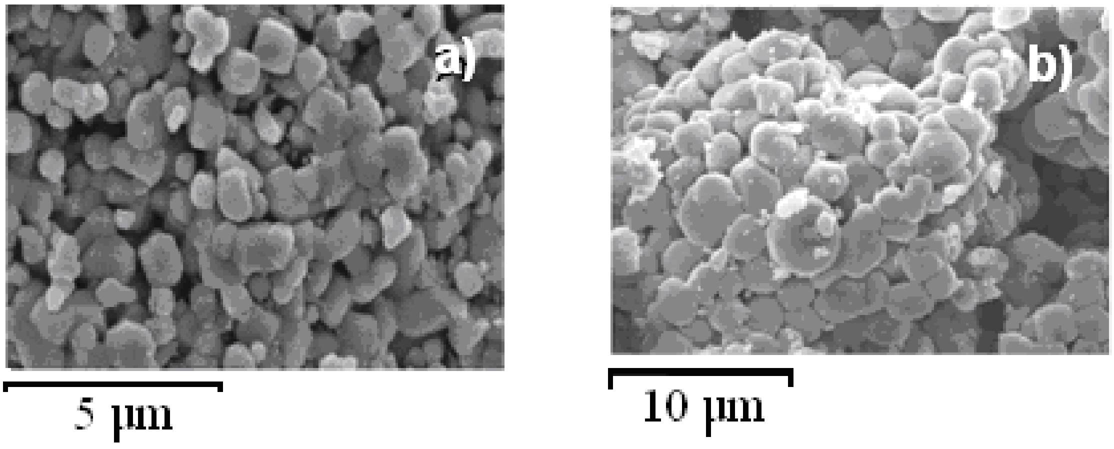

Fig. 1. Scanning electron micrographs of the $CaTiO_3Pr$ films deposited by sol-gel technique: a) lower immersion time; b) higher immersion time.

3.2. SYNTHESIS AND CHARACTERIZATION OF DEPOSITS BY SPRAY PYROLOYSIS TECHNIQUE

High quality $CaTiO_3Pr$ coating was obtained also by spray pyrolysis technique. The thickness of the film has several micrometers recorded by means of the XRD measurements. The pattern recorded for sprayed films depict the beginning of the crystallization process at 550 ºC after the (121) direction (Fig. 2). The average size of the crystallites at 1000 ºC is about 75 nm using the Scherrer's equation.

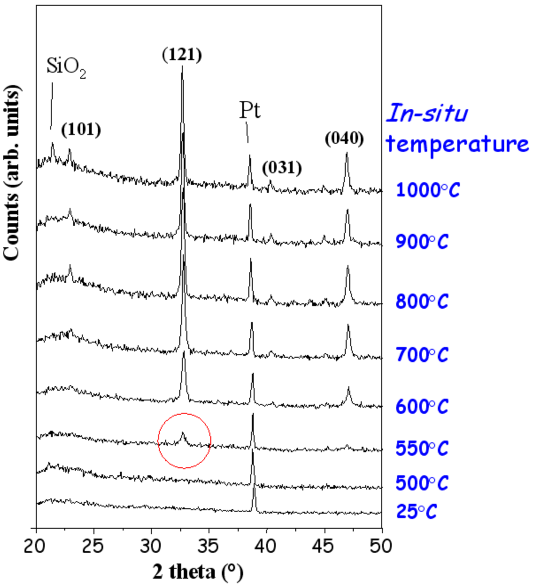

Fig. 2. XRD patterns of the $CaTiO_3Pr$ film deposited by spray pyrolysis technique.

After the heat treatment, the films were translucent depending on the amount of deposited matter. The texture of the as-deposited mineral is changed with increasing temperature (Fig. 3) [10].

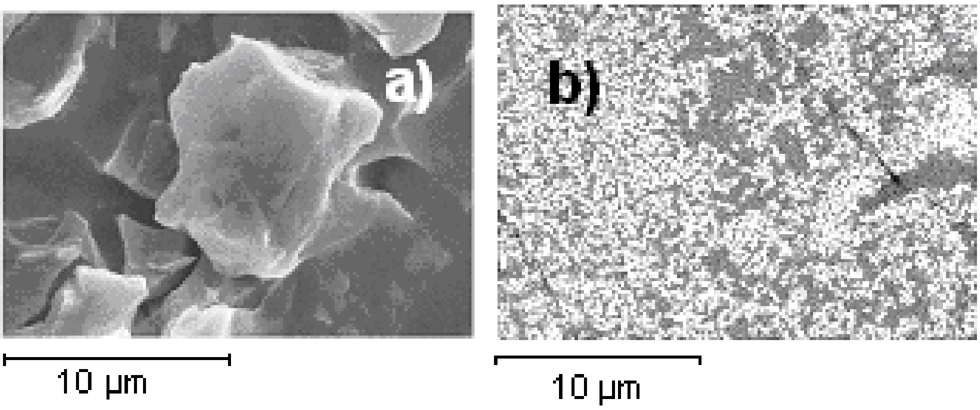

Fig. 3. SEM micrographs of the $CaTiO_3Pr$ film deposited by spray pyrolysis technique and heated at a) 800 ºC and b) 1000 ºC.

The film heated at 800 ºC presents a step-like structure with ladders piling up perpendicularly to the substrate. After heating at 1000 ºC the surface morphology became uniformly smooth with a good adherence.

3.3. SYNTHESIS AND CHARACTERIZATION OF DEPOSITS BY ELECTROCHEMICAL TECHNIQUE

Initially the electrical conductivity was measured at 13.51 mS/cm but at the end of the experiments it is ranged between 19 and 20.5 mS/cm. A slowly increasing of the σ parameter can be observed during the deposition processes. Therefore, the amount of electrical charge which is lead through the electrolyte solution is approximately constant.

The chrono-amperometry technique was chosen to prepare the $CaTiO_3Pr$ thin films. The standard electrode potentials for each component were brought from the literature such as, E_0 (Pr^{3+}) = - 2460 mV, E_0 (Ca^{2+}) = - 2868 mV and E_0 (Ti^{4+}) = - 1630 mV. First, the open circuit potential measurement of the system is performed to determine the free potential (P_1) which started the chrono-amperometry measurement. To deposit first sample during 130 min at 0 ºC temperature, P_1 from OCP is -180 mV and the first step potential (P_2) was fixed at -2900 mV to allow every element to deposit at its standard electrode potential. The second experiment takes 130 min deposition times at 30 ºC, P_1 was recorded at -160 mV and P_2 was fixed at the same value, -2900 mV.

Fig. 4 shows the first stage of nucleation centres creation, the second stage represents the crystalline grains formation and the third stage shows the crystalline grains development. At 0 °C, the grains develop quickly at higher current density values from the negative range (Fig. 4-black curve). This moment is favourable to obtain a homogeneous inorganic composite coating. At 30 °C the grains develop slowly at lower current density in the same negative range (Fig. 4, blue curve). The very low current densities can favours the absorption of H^+ onto the cathode surface, and then the surface appearance could be: powdery, brittle, mat.

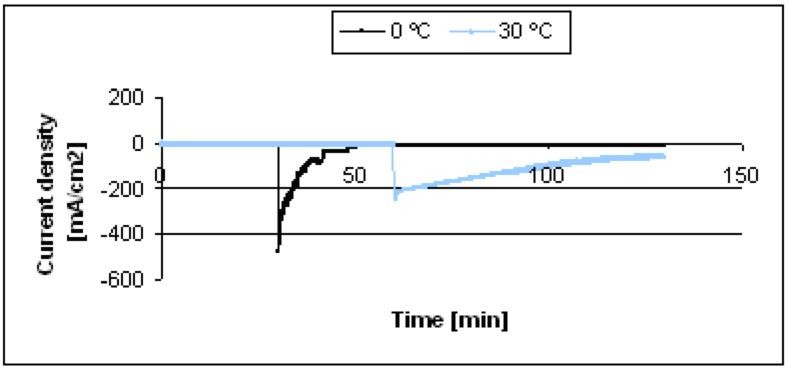

Fig. 4. The electrochemical deposition by chrono-amperometry method of $CaTiO_3Pr$ compounds: at 0 °C - 130 min (black curve) and at 30 °C - 130 min (blue curve).

The surface morphology of $CaTiO_3Pr$ films depends mainly on the working conditions. The surface structure of $CaTiO_3Pr$ films plated at two different stages of deposition is shown in Figs. 5 and 6 [12]. The microscopic analysis shows the formation of sporadically tetrahedral shape crystallites with small sizes onto copper substrates which are specific to $CaTiO_3Pr$ mineral at 0 °C (Fig. 5). The quickly current density increase will determine an aspect more homogeneous and uniform of the films.

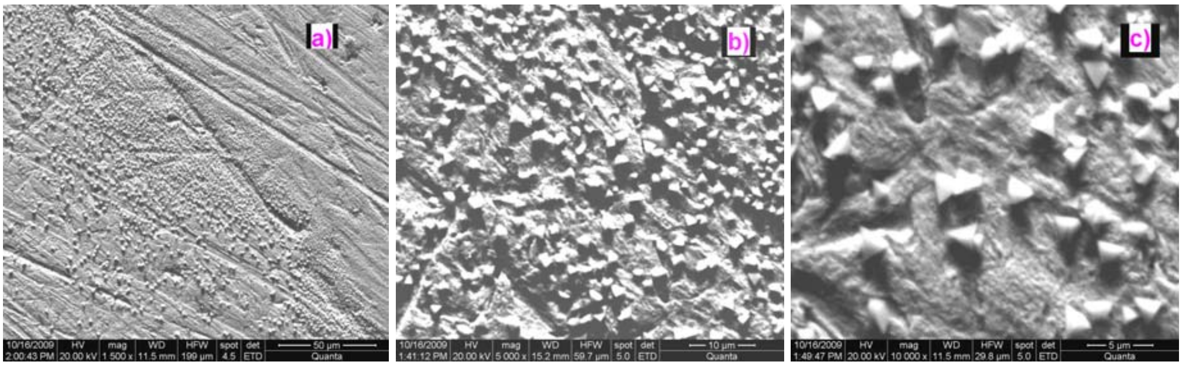

Fig. 5. SEM micrographs of $CaTiO_3Pr$ deposit during 130 min at 0 °C.

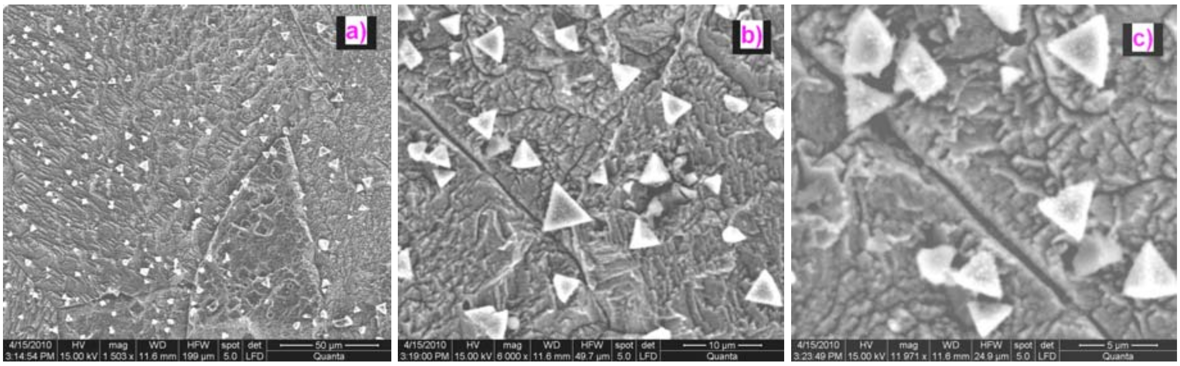

Fig. 6. SEM micrographs of a $CaTiO_3Pr$ deposit during 130 min at 30 °C.

Temperature increasing (to 30 °C) is favourable to films developing and growing. The crystallite sizes are higher against those obtained at 0 °C (Fig. 6) but they have the same tetrahedral geometrical shapes. The crystallisation process is proportional with temperature.

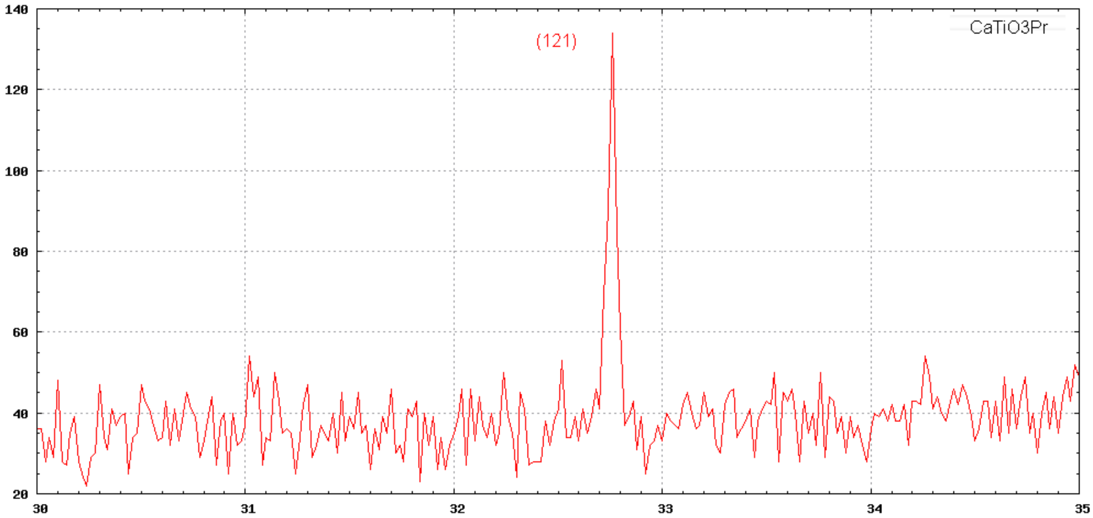

Fig. 7. XRD pattern of $CaTiO_3Pr$ deposit by electrochemical method at 30 °C.

XRD pattern depict the above crystallisation of the mineral complex after (121) crystallographic direction (Fig. 7). The results are confirmed by the XRD pattern from Fig. 2. The (121) crystallographic plane is developed in the angular domain between 32° and 33° as 2θ. Therefore, a film with a broad layer thickness was developed due to the great number of nucleation processes which took place.

4. CONCLUSIONS

In the present work, the $CaTiO_3Pr$ inorganic coatings have been prepared by electrochemical deposition of Pr^{3+} particles onto copper substrates from an acidic electrolyte solution. The obtained results were compared and discussed with those recorded by sol-gel and spray pyrolisis techniques. The chrono-amperometry technique was chosen to prepare the $CaTiO_3Pr$ thin films. The grains develop quickly at higher current density values and 0 °C from the negative range. A homogeneous composite coating was obtained.

The grains develop slowly at lower current density at 30 °C. The very low current densities can favors the absorption of H^+ onto the cathode surface, and then the surface appearance could be: powdery, brittle, mat.

The surface morphology of $CaTiO_3Pr$ films depends mainly on the working conditions. The microscopic analysis shows the formation of sporadically tetrahedral shape crystallites with small sizes onto copper substrates which are specific to $CaTiO_3Pr$ mineral at 0 °C.

Temperature increasing is favorable to films developing and growing. The crystallite sizes are higher than those obtained at 0 °C, but they have the same tetrahedral geometrical shapes.

The crystalline feature of $CaTiO_3Pr$ mineral is depicted by the crystallites increasing after (121) direction which is confirmed by the XRD spectra obtained by the above mentioned deposition techniques. The Pr^{+3} ions occupy single well-defined crystallographic site in the orthorhombic structure of $CaTiO_3Pr3^+$.

The performances of prepared films are strongly influenced by the preparation conditions, the possibly applied thermal treatments them influencing both crystalline structure and/or microstructure.

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