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Electrical properties and humidity sensor characteristics of lead hydroxyapatite material

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ABSTRACT

Crystalline lead hydroxyapatite is obtained by direct precipitation from aqueous solution, the method being easy, fast and reproducible. The synthesis route which does not involve sodium salts or sulfates makes the material suitable for applications in catalysis. The electrical characteristics of lead hydroxyapatite material treated at different temperatures, made us focus on the analysis of the influence of water vapors upon the electrical characteristics. Thus, the electrical response to humidity adsorptive processes of lead hydroxyapatite material suggested us to analyze the material characteristics in terms of its use as a humidity sensor. The hydrophilic properties of lead hydroxyapatite material are reflected especially in high sensitivity and reduced time of response of the humidity sensors but also in long time of recovery, which suggests that $Pb_{10}(PO_4)_6(OH)_2$ material can be used for humidity sensors specialized in monitoring fluctuating humidity environments.

1. Introduction

Apatite is a group of phosphate minerals, one of the few produced and used by biological systems [1,2]. The prototype $Ca_{10}(PO_4)_6F_2$ was reported in 1930 by Náray-Szabó [3] and Mehmel [4]. Since then, hundreds of natural and synthetic apatites of $A_{10}(BO_4)_6X_2$ (A = Ca, Sr, Ba, Pb; B = P, As, V, Si, X = F, Cl, OH) formula were reported [5–8]. Many of them found application in fertilizers industry, catalyses, biomedicine and dentistry, as phosphors, ceramic membranes, in environmental remediation etc. [9–14]. Apatite also has been proposed as a backfill material in geologic repositories for nuclear waste disposal and as a nuclear waste form [15–17].

Lead hydroxyapatite, $Pb_{10}(PO_4)_6(OH)_2$, is an interesting compound, since it precipitates directly crystallized from aqueous solution, being a sparingly insoluble phase. Thus, it poses a high specific surface, which makes it a good adsorptive material [18–20]. It also found in catalytic applications in the oxidation of ethane [21], oxidative coupling of methane [22] or dehydration of ethanol [23].

The porous materials as the lead hydroxyapatite can be also useful in environmental monitoring applications, especially as active materials for humidity and gas sensors [24,25]. From this perspective, an analysis which highlights how the lead hydroxyapatite material changes its characteristics by different thermal treatments can be extremely useful.

The objective of the current analysis was to point out the influence of the humidity on the electrical characteristics of lead hydroxyapatite material. Another objective of this study was to investigate the way in which Pb presence is reflected in the properties if the hydroxyapatite material, especially on the electrical ones. This analysis is essential for optimizing the properties in order to use it in various applications [26]. To our best knowledge, the dielectric and humidity sensor properties of lead hydroxyapatite were not reported and no information related to the influence of the frequency and annealing temperature on the electrical and the humidity sensor properties was known.

In the next sections the preparation method, structural, electrical and humidity properties of lead hydroxyapatite material treated

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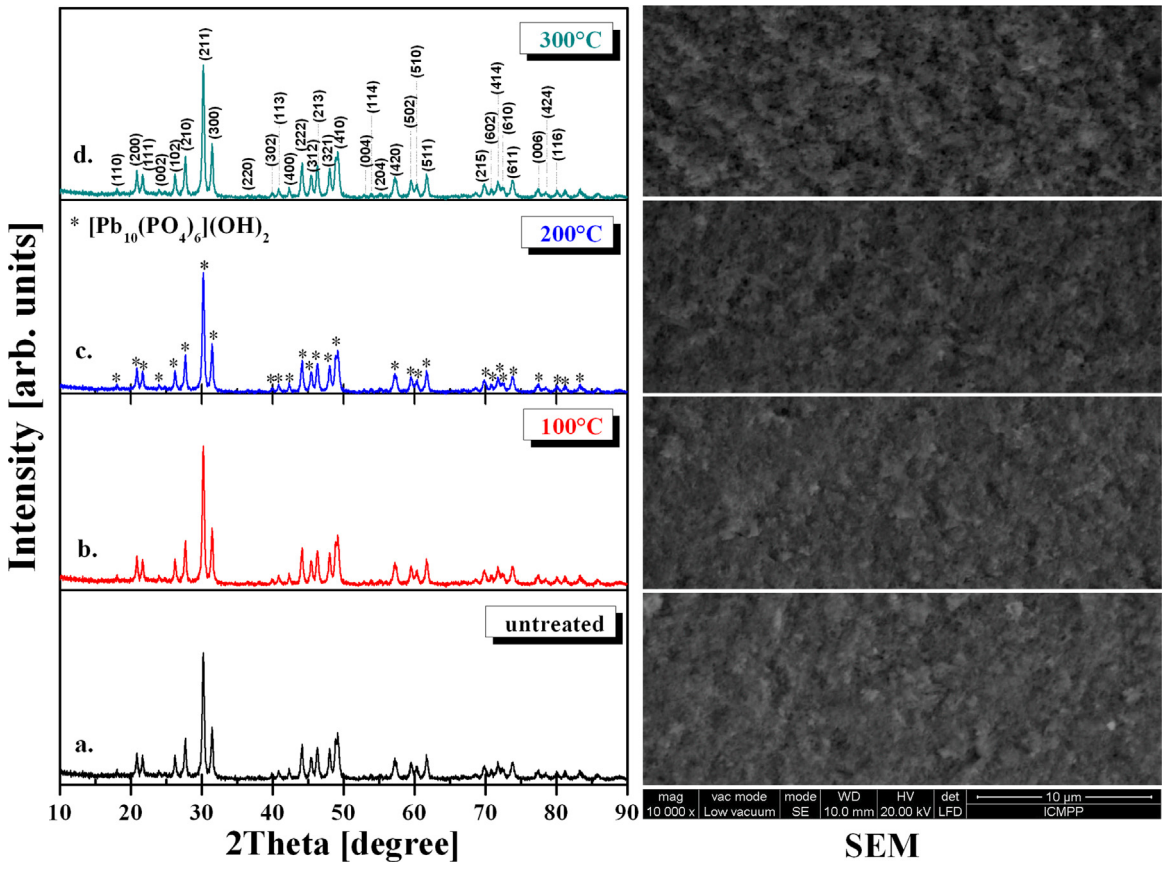

Fig. 1. XRD patterns and SEM characteristics of lead hydroxyapatite material treated at different temperatures.

at different temperatures are presented. In the second part, the characteristics of resistive and capacitive humidity sensors with lead hydroxyapatite as active material are analyzed.

2. Preparation and characterization of the material

The amount of 27.8110 g $PbCl_2$ (10 mmol) were dissolved in distilled water at 70 °C under continuous stirring. Another solution obtained by cold dissolution of 7.9263 g $(NH_4)_2HPO_4$ (6 mmol) in distilled water is also prepared. The phosphate solution is added dropwise to the lead one, while white precipitate forms in the entire volume. After about 1 h of ageing, the precipitate is filtered (G4 filtering crucible) and washed several times with distilled water. The precipitate was dried overnight in air and was then thoroughly milled in an agate mortar. The obtained product is already crystallized and poses a high specific surface, making it a good adsorptive material [20].

This method, derived from the one used by Brückner et al. [27] does not involve sodium (which should be avoided in the catalysts preparation) and it is easy to be reproduced in any chemical unit. The other methods reported in the literature are rather complicated and energy consuming [28–33].

In order to perform electrical measurements, lead hydroxyapatite powders was uniaxially pressed into a cylindrical mold with 6 mm diameter, using a pressing force of 2 ton the thin disc-shaped samples (pellets) were obtained. In order to study the influence of annealing on the structural and electrical properties of lead hydroxyapatite, the compacted disc-shaped samples were heat-treated 6 h in air at 100 °C, 200 °C and 300 °C for each treatment. The cooling process of the samples after each heat treatment was done slowly, in the sintering furnace [34].

The microstructure and phase components were investigated by X-ray diffraction using a Bruker AD8 Advance diffractometer using CuKα radiation at (λ = 1.5405 Å) a scanning speed of 3°/min and an accelerating voltage of 40 kV.

One could observe that lead hydroxyapatite, $Pb_{10}(PO_4)_6(OH)_2$, facile precipitates from solution directly crystallized as a pyromorphite-like compound (space group $P6_3/m$). The lattice parameters, calculated based on the Rietveld method ($a = b = 0.9876(5)$ nm, $c = 0.7431(6)$ nm), fit the literature reports [6,27,29].

The structure is maintained during sintering at different temperatures, as shown in Fig. 1. This is in line with the work of Sugiyama et al. [31], which reports the limit of stability of the compound in air of 700 °C.

X-ray diffraction shown in Fig. 1 (PDF card number 08-0259) confirms that both untreated and treated samples contain only lead hydroxyapatite phase, outlining the fact that the material remains stable after the thermal treatment. From X-ray diffraction analysis of the samples it is apparent that they are a single phase with the most intense emergence peak (2 1 1) at 30°, similar results being reported by other authors [33,35]. The scanning electron microscopy (SEM) investigations of the fracture surfaces of the samples annealed at various temperatures were performed at room temperature by TESCAN VEGA II SBH device. It is evident that the morphology of the annealed samples has a fine structure with intergranular pores which can favor the adsorption and condensation of water vapors of the active surface. The SEM micrographs of lead hydroxyapatite material (see Fig. 1 – right side) highlight a smaller influence of the sintering temperature on the microstructure, outlining the stability of the material in relation to the thermal influences.