Novel synthesis and characterization of crystalline fluorapatite from Moroccan phosphogypsum waste

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Abstract. In the present study, phosphogypsum waste (PG) was utilized to synthesize fluorapatite (FAP) via a simple precipitation method. The FAP was prepared using a novel mixing technique with anhydrite obtained from PG and phosphoric acid solution in the presence of pure fluoride ammonium in a Teflon reactor. The characteristics of the prepared FAP were investigated with various methods including Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). The FAP derived from PG exhibited a hexagonal structure with a particle size ranging from 1.5 to 9 μm along with a high purity. FAP also showed an excellent Ca/P ratio equals to 1.67. These results proved that the FAP was successfully synthesized from phosphogypsum waste.

Keywords: fluorapatite / phosphogypsum / materials / mechanochemical

1 Introduction

Phosphogypsum (PG) is an acidic waste produced by the phosphate fertilizer industry during the production of phosphoric acid from phosphate rock. The waste is composed mainly of gypsum and the phosphorus content is usually below 1%. Large stockpiles of phosphogypsum are dumped, often into water supplies throughout the world. The worldwide production of phosphogypsum was 120–150 million metric tons in 1980 [1–3]. The Jorf Lasfar plant in Morocco pumps 25 000 tons/day of phosphogypsum into the Atlantic Ocean when operating at nominal capacity [4], which represents a huge environmental concern regarding its management. Therefore, many studies proposed different methods of purifying and minimizing PG's environmental impact, such as leaching solutions [5–8].

This paper describes a novel synthesis process of fluorapatite (FAP) from PG waste. FAP is a member of the apatite mineral group and even considered the most thermodynamically stable mineral of the apatite group. Its chemical formula denoted $Ca_5(PO_4)_3F$, and this mineral considered as an important mineral since it is a promising candidate for near infrared laser when doped with transition metal ions such as Mn$^{2+}$ [9,10].

The precipitation synthesis of FAP offers several advantages over other techniques including fast reaction, rapid heating and excellent thermal stability, which contribute to it being one of the most effective processing methods for nanomaterials [11–14].

The proposed precipitation synthesis is considered as a substantial approach for synthesis of FAP crystals. This process is fully described in this research paper. It should be noted that several techniques have been employed to identify the crystalline structure, composition and morphology of the prepared FAP by XRD (X-Ray Diffraction Spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy) and SEM (Scanning Electron Microscopy) coupled with EDS (Energy-Dispersive Spectroscopy).

2 Materials and methods

The phosphogypsum was provided from the Moroccan phosphate industry in Morocco. The collected PG was first oven dried at 80°C, then milled and sieved through sieve sizes of about 80 μm. The major components and traces of the PG were identified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as illustrated in the
Table 1. Chemical composition of phosphogypsum derived from Moroccan phosphate (wt%).

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>S</th>
<th>P</th>
<th>MO</th>
<th>Al</th>
<th>Fe</th>
<th>K</th>
<th>F</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>23.05</td>
<td>18.04</td>
<td>0.40</td>
<td>0.14</td>
<td>0.07</td>
<td>0.58</td>
<td>0.14</td>
<td>0.12</td>
<td>0.10</td>
<td>0.10</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Tab. 1. According to this data, the main components of the PG were CaSO\(_4\) (expressed as Ca and S), P, MO (organic matter) Al, Fe, K, F, Mg, Na and Si.

2.1 Preparation of the stoichiometric fluorapatite powder

In order to prepare the FAP, orthophosphoric acid solution (H\(_3\)PO\(_4\)), pure fluoride ammonium (NH\(_4\)F), and anhydrite (CaSO\(_4\)) in the presence of sodium hydroxide (NaOH) were used, respectively, as P, F, and Ca precursors with a Ca/P ratio equals to 1.67.

First, the anhydrite was obtained through the dehydration process of phosphogypsum using a concentrated sulfuric acid 67% [11]. During the second step, the quantities of about 1.32 moles of H\(_3\)PO\(_4\) and 0.44 moles of pure NH\(_4\)F in 1.50 L of the distilled water were mixed and added to 2.20 moles of the prepared anhydrite. The suspension was stirred continuously and the pH was adjusted to 9–10 using NaOH. The resulting solutions were vigorously agitated at 500 rpm for 48 h. The FAP can be obtained by the following equation (1):

\[
10\text{CaSO}_4 + 6\text{H}_3\text{PO}_4 + 2\text{NH}_4\text{F} \rightarrow \text{Ca}_{10}\cdot(\text{PO}_4)_6\cdot(\text{F})_2 + 9\text{H}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4.
\]  

The resultant powders were dried at 105°C for 24 h. Thereafter, the FAP was calcined at 600°C and at 900°C during 3 h for each calcination. Chemical properties, phase composition, chemical structure and size, and morphological properties of the FAP nanoparticles were characterized by physico-chemical techniques of solid state such as XRD, FTIR and SEM/EDS.

2.2 Materials characterizations

The crystalline structure of the prepared FAP was characterized using an X-ray diffractometer (XRD) XPert Pro MPD of panalytical using Cu Kα radiation (λ = 1.54 Å) at a scanning rate of 0.02°/s for a 2θ range of 5–80°. The morphology and the general chemical composition of FAP were identified by Scanning Electron Microscopy (SEM) (FEI Quanta 200 ESEM) coupled with Energy-Dispersive Spectroscopy (EDS). Fourier Transform Infrared Spectroscopy was performed to investigate the distribution of functional groups on the surface by FTIR-8400S. Analysis ICP was performed by AES Jobin Yvon Ultima 2.

3 Results and discussion

3.1 XRD analysis

Figure 1 depicts the XRD pattern of the prepared fluorapatite particles dried at 105°C and calcined at 600°C and 900°C. Diffraction peaks registered at 2θ (°) = 25.83°, 28.02°, 29.17°, 31.79°, 32.96°, 34.13°, 39.94°, 46.84°, 48.19°, 49.52°, 50.69°, 51.47° and 53.06° were attributed to (002), (102), (210), (211), (300), (202), (310), (222), (312), (213), (321), (410) and (004) are characteristics of pure hexagonal structural fluorapatite according to JCPDS card no. 15-876. Broad peaks were observed for dried FAP at 105°C. However, as calcination temperatures increased beyond 600°C, there was a clear change in the height and width of the peaks: they became sharper at 900°C owing to well-crystallized phase. Therefore, the increase of calcinations temperatures resulted in a higher crystallinity [15,16].

Fig. 1. XRD patterns of fluorapatite dried at 105°C (a), calcined at 600°C (b) and 900°C (c).
Fig. 2. FTIR spectra of fluorapatite dried at 105°C, calcined at 600°C and 900°C.

Fig. 3. SEM images of fluorapatite dried at 105°C (a), calcined at 600°C (b) and 900°C (c).
3.2 FTIR analysis

Figure 2 shows FTIR spectra of the FAP dried at 105 °C and calcined at 600 and 900 °C. The spectra showed typical apatite phosphate vibration bands located at 570 (ν4), 603 (ν4), 960 (ν1), 1047 (ν3) and 1092 cm⁻¹ (ν3) [16]. The absorption band assigned to CO₃²⁻ group was detected at 1420 cm⁻¹ (ν1) [16]. The carbonate species have originated from organic matter included in PG. It is believed that carbon dioxide might have originated from atmospheric absorption; this band disappeared with the increase of the temperature [16,17]. The absorption peak observed at 1626 (δ1) and 3413 cm⁻¹ (ν1) for the sample dried at 105 °C is belonging to water included in the samples and/or absorbed in the KBr pellet. This band disappeared as the temperature increased.

Figure 2a shows that the FAP samples dried at 105 °C were agglomerated due to the presence of water (suspension). In addition, the micrographs give us an idea about agglomerates of particles interconnected, in different ways, into structures of different forms, morphology and distribution, the FAP calcined at 600 °C has very similar dimensions to those of enamel crystals isolated from rat incisors (Fig. 3). The FAP calcined at 900 °C was composed of hexagonal particles with high symmetry; the surfaces of the hexagonal particles are extremely smooth with obvious defects. Particle size ranges from 1.5 μm to 9 μm.

The technique EDS determines the composition of the FAP materials by measuring concentration ratios of Ca, P and F from various parts of sample. This confirmed that a very homogeneous distribution of components is formed during different step of preparation. The formation of fluorapatite can confirm that the Ca/P ratio value of prepared FAP was 1.77 according to EDS results given in Figure 4. The chemical analysis (see Tab. 2) shows that the Ca/P ratio is equal to 1.667 which is close to 1.67.

Again, to check the composition of as-synthesized FAP, EDS was performed and demonstrated in Figure 4. The EDS result indicated that we synthesized FAP.

### Table 2. Chemical analysis of fluorapatite particles dried at 105 °C (wt%).

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>P</th>
<th>F</th>
<th>Na</th>
<th>Ba</th>
<th>Mn</th>
<th>Ti</th>
<th>Pb</th>
<th>Sr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG</td>
<td>23.05</td>
<td>0.39</td>
<td>0.12</td>
<td>0.10</td>
<td>66</td>
<td>3.6</td>
<td>996</td>
<td>1.66</td>
<td>811</td>
<td>5.76</td>
</tr>
<tr>
<td>Prepared FAP</td>
<td>31.17</td>
<td>14.29</td>
<td>5.24</td>
<td>0.32</td>
<td>43.22</td>
<td>0.87</td>
<td>879</td>
<td>1.06</td>
<td>618</td>
<td>3.19</td>
</tr>
</tbody>
</table>

4 Conclusion

The experimental results obtained for the synthesis of fluorapatite led to the followings:
- The synthesis proceeds in several steps. In the first step, anhydrite was prepared from phosphogypsum. After the strong phosphoric acid and fluoride ammonium pure were added to forming the fluorapatite powders.
The FAP material was characterized by solid-state techniques of characterization. In this case, XRD, FTIR and SEM/EDS were selected to be used as characterization methods of the samples.

The XRD spectrum showed that the prepared FAP was pure and had a hexagonal structure.

The FTIR showed a disappearance of the CO$_3^{2-}$/CO$_2$ band at 900°C.

The crystallite size of the fluorapatite nanoparticles increased with increasing temperature.

The ICP of FAP showed the existence of Ca, P and F elements and the Ca/P ratio value of 1.67 which confirm the formation of fluorapatite.

References


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