



Synthesis and characterization of nano-sized hydroxyapatite and doped with some rare earth elements from phosphogypsum waste

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Abstract : Phosphogypsum (PG) derived from the manufacturing of phosphoric acid by wet process method was converted to nano-particle hydroxyapatite (HAP). Also, the effects of the calcination temperature and the doping with some rare earth elements (La and/or Ce) on the structure of the produced HAP particles were studied. The produced samples were characterized by scanning electron microscope (SEM), Transmission electron microscope (TEM), IR absorption, X-ray diffraction and the thermogravimetric analysis (DTA&DTG). The results of characterization show that PG converted to nano-particle HAP and crystallize in the form of hexagonal structure. The crystalline formation increased by heat treatment up to 900° C. Also, it is found that the doping with different percentage of La or Ce improved the crystallinity of the doped hydroxyapatite. The thermogravimeter analysis shows that the doping of HAP increases the thermal stability and other produced samples and the doped and undoped samples are thermally stable up to 1000 °C.

1. Introduction

Due to the huge amounts of phosphogypsum (PG) produced from the manufacturing of phosphoric acid by using the wet –process route, several units of production are facing the threat of shut down by environmental authorities because of their gypsum disposal⁽¹⁾. This problem not only for production of H₃PO₄, but also in the case of citric acid manufacturing (citrogypsum) and tartaric acid (Tartogypsum). Therefore, different trails to minimize the pollution by introducing PG⁽²⁾ in some uses were done during past few decades. Since 1989, Hanna et al suggested different utilization from the phosphogypsum. This trials included the production of ammonium salt⁽³⁾, the using of PG as adhesive material for polyamide⁽⁴⁾, and production of potassium sulphate⁽⁵⁾. As continuation of this policy, the present work was aimed to prepare hydroxyapatite (HAP) in nano- sized and to increase the value of the HAP; some rare elements were doped in the nano- particle of HAP.

Among the different biomaterials, HAP gained a special attention because it has similarities with some inorganic mineral component of bone beside it processes high bioactivity effects. Also, the synthetic HAP have good mechanical properties, non-toxic, inflammatory response, pyrogenic response, or fibrous tissue formation

between implant and bone and has high ability to bond directly with the host bone. Since the use of HA for the first time in 1981 for periodontal lesion filling, different research were done to improve the properties of HAP, through the methods of preparation or modifying their structure and properties⁽⁶⁾. The modification HAP enhances to use the produced particle in different purposes. As example of this modification increase the surface area of HAP of which can provide large interfaces giving high catalytic activity and great adsorption capability in the catalysis and separation of some toxic cations⁽⁷⁾. As the physical, chemical, mechanical and biological properties of HAP are controlled by its crystal structure and composition, substitution of Ca^{+2} with other metal ions is one of the effective ways to improve the properties of HAP. The doping of some cations such as Ag^+ , Cu^{+2} , and Zn^{+2} in HAP structure have great effects on the crystallinity, morphology and lattice parameters⁽⁸⁾

Rare earth doped HAP nanoparticles shown different advantages such as long fluorescence lifetime, high quantum yield, sharp emission peaks, color tanning and good resistance to photo bleaching from environmental and other factories. Several research were carried to doped some rare earth metal such as Ce^{+3} , Pr^{+3} , Nd^{+3} , Sm^{+3} , Eu^{+3} , Tb^{+3} , Dy^{+3} , Tm^{+3} and Yb^{+3} ⁽⁹⁾.

On other hand the codoping of rare earth elements such as Eu^{+3} / Gd^{+3} can enhance the NIR emission. Doping HA with Eu^{+3} caused decrease in the size of the particles⁽¹⁰⁾ which by turn effects on the solubility as well as the biological properties to some extent

2. Experimental:

2.1. Material

The starting material in this work was the phosphogypsum waste (PG) produced from the manufacturing of phosphoric acid by dissolving the phosphate rock in sulphuric acid. The chemical analysis of the PG sample shows that it contains 9.49 H_2O , 18.20 CaO , 41.39 SO_3 , 0.1 Fe_2O_3 , 0.2 MgO , 0.8 P_2O_5 , about 0.2 Fluorine and about 141×10^{-6} total rare earth elements⁽¹¹⁾. Absence of Cd which is the more pollutant element favors the utilization of this waste product.

Phosphoric acid (85%) as a source of phosphorous and ammonia solution for PH adjustment at 11, La_2O_3 and CeCl_3 as source of the rare earth cations.

2-2 The method of preparation

Hydroxyapatite was prepared according to the following equation.



This method was described elsewhere⁽³⁾

The prepared hydroxyapatite was doped indivdly by two rare earth elements (La or Ce) during the preparation. Three samples including rare earth elements were prepared using different percentages from the doped elements (0.25, 0.5, 0.75wt %) to study the effects of the doping on the crystallinity and the structure of the parent hydroxyapatite. The effects of the calcination temperature also were studied by exposing the prepared samples to 500, 700, and 900°C

2-3:- Characterization of the prepared samples:

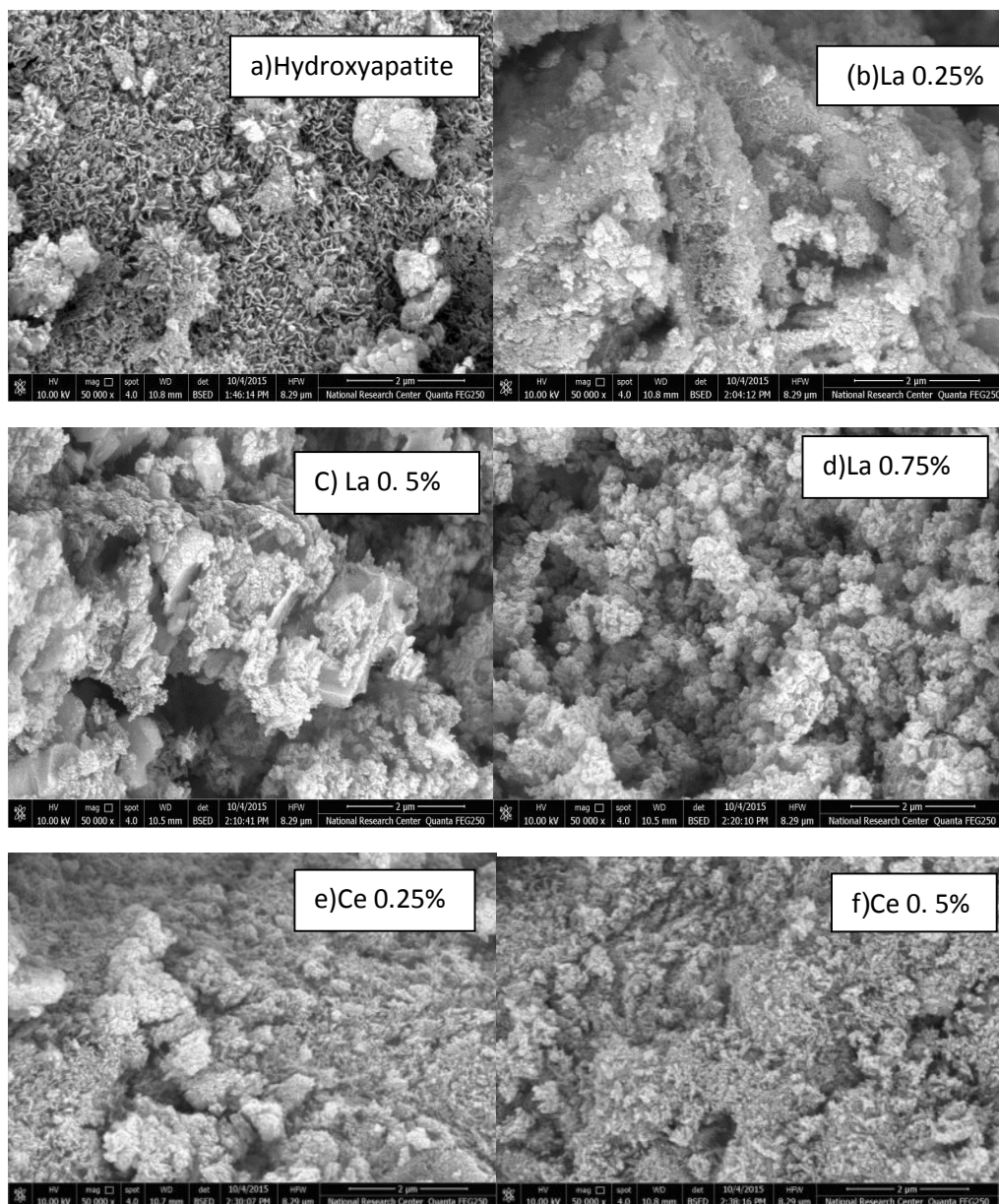
The prepared samples were characterized by using different methods. The micrographs of the prepared samples and at different calcinated temperature were carried by Scanning electron microscope (SEM) Joel-JAX-840 A, Japan) with electron probe microanalyser and the morphology and the particle size were examined by Transmission electron microscope (TEM,)JEOL JEM- 1230 at 100 Kev. Infrared absorption spectra (IR) were performed by KBr disc technique and using a Fourier transformer infrared spectrometer (Nexus670 FTIR USA) in the range between 400 to 4000 cm^{-1} . The formed phases were studied by using x-ray technique (XRD). The x-ray diffraction was carried by using Bruker D8 advance diffractometer (Germany) using Cu K radiation. The thermal analysis of the dried samples was performed by USA Perkin. Elmer thermogravimetric up to 1000 °C with rate having 10 °C/m.

3. Results and Discussion:

The structure and the chemical analysis of the waste phosphogypsum used in this work were investigated elsewhere⁽³⁾. The investigation shows that the PG samples are a one phase of gypsum dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. [Jepds (06-0047)]. The dried prepared HAP and that doped with the more important rare earth element La or Ce were characterized by using different techniques:-

3.1. SEM of the hydroxyapatite and doped with La, Ce

The micrographs of the prepared sample (pure HAP, and doped with La or Ce) were shown in Fig. 1. The hydroxyapatite formed in rod like shaped structure with average size of 10-20 nm. Some of nano-metric primary particles agglomerated tightly into aggregates of various size and shape (Fig. 1a). The micrographs of the HAP doped with La were shown in (Fig. 1b–d), corresponding to La contents of 0, 0.25, 0.5, and 0.75 wt%, respectively. The treated HAP with La shows a semicoherent structure formed by hard agglomerates of rods like particles. (Fig. 1b). The hard agglomerates of HAP become loose with increasing La ratio wt % (Fig. 1c, d). When La content was 0.75 wt %, a highly porous structure with very fine pores formed with high grouping of monolithic particles was obtained. This observation is in agreement with that reported in.⁽¹²⁾



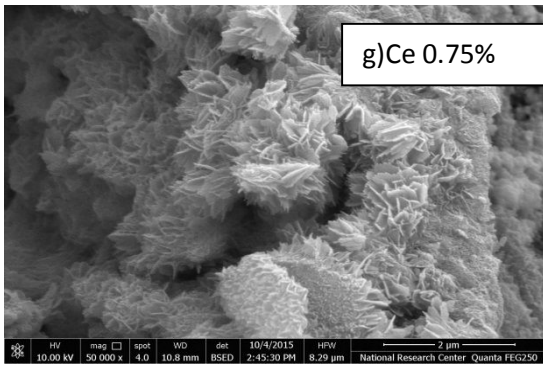
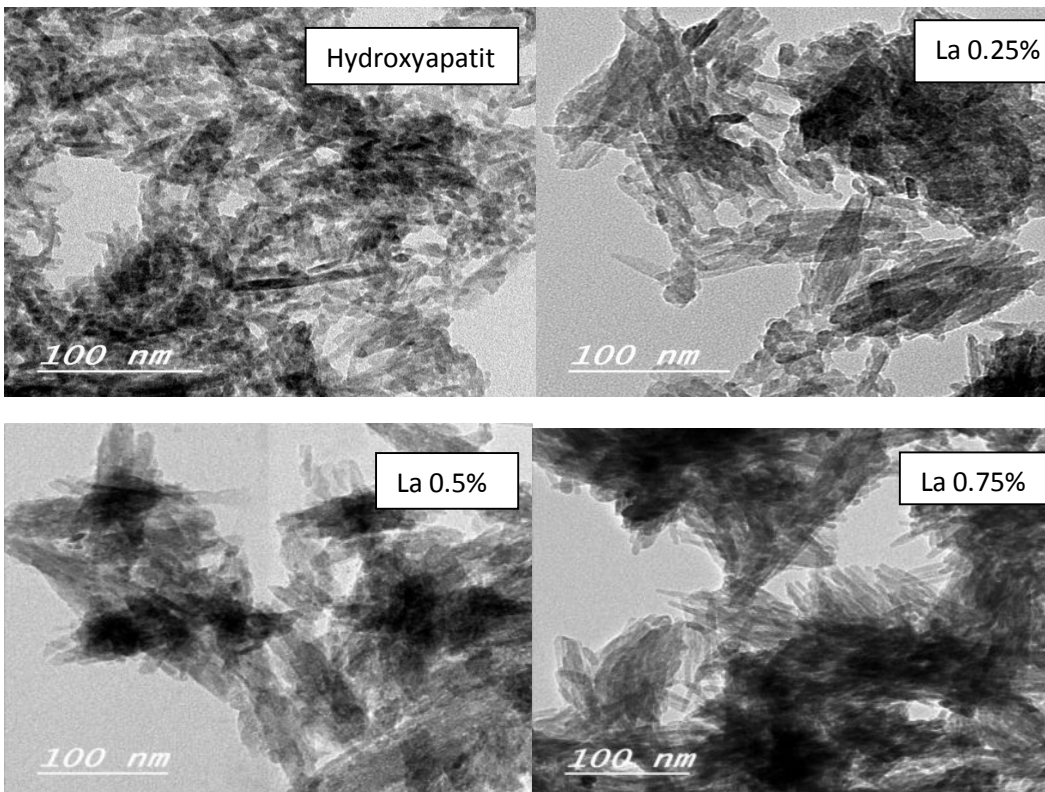


Fig 1: The SEM of the doped and undoped HAP samples (La or Ce =0.25,0.5,0.75%)

In the case of doping with Ce Fig. (1e-f) the arrangement of the particles become more uniform and dense with increasing in particle size. Also, the structure formed a porous structure but not with fine pores as that formed with La addition.

3.2. TEM of the hydroxyapatite and doped with La and Ce

Fig.2 shows the TEM micrographs of the pure prepared HAP and that doped with La or Ce with different ratios. The micrographs reveals a hollow rod like shaped particles describing a homogenous HAP nano-particles as confirmed previously from SEM investigation, the width of the formed rods is in the range of 10 to 20 nm as clearly shown from Fig.2a. Certain agglomeration of rods with increasing in the length of rods was observed with increasing La content as shown from Fig. 2. This agglomeration between formed rods is attributed to large surface area and energy associated with nano-particles. Ce addition affects vigorously on the morphology of HAP rods causing some distortion



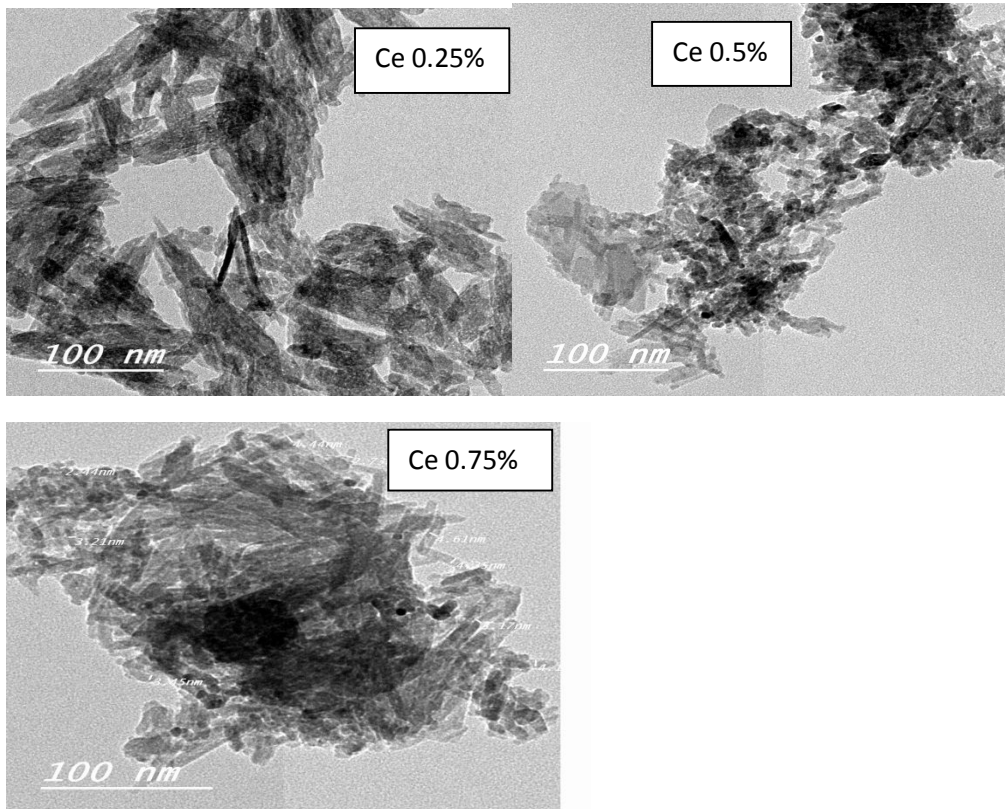
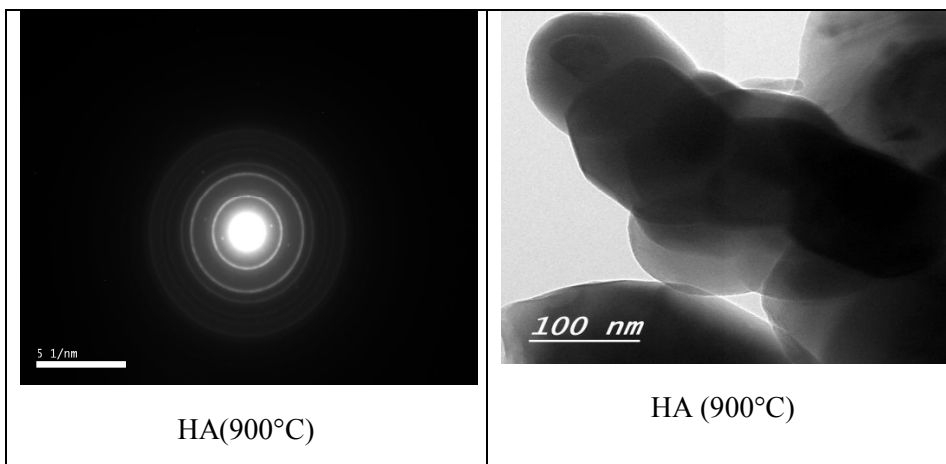


Fig 2: The TEM of the doped and undoped HAP samples (La or Ce =0.25, 0.5, 0.75%)

3.3. TEM after heating at 900°C

The morphology of calcined samples of HAP and doped with La or Ce at 900° C are depicted in Fig. 3.

The micrograph of HAP showed formation of stacked crystallites, with hexagonal structure forming big size crystal in the range from 100-200nm. While the un agglomerated crystals are in the range of 25 nm. In case of calcined HAP doped with La, TEM micrograph and its corresponding diffraction pattern showed an improvement in crystalline structure while still with large size from 200-500 nm and the agglomeration is the predominant characteristic to the formed crystals or particles. The morphology of the calcined HAP doped with Ce showed a smaller crystallite size formation in range from 25-100nm with less agglomeration compared to that of samples treated with La and the polycrystalline structure can be observed from the corresponding diffraction pattern as shown latter. For all the prepared samples the crystals in hexagonal structure are formed by calcination at high temperature.



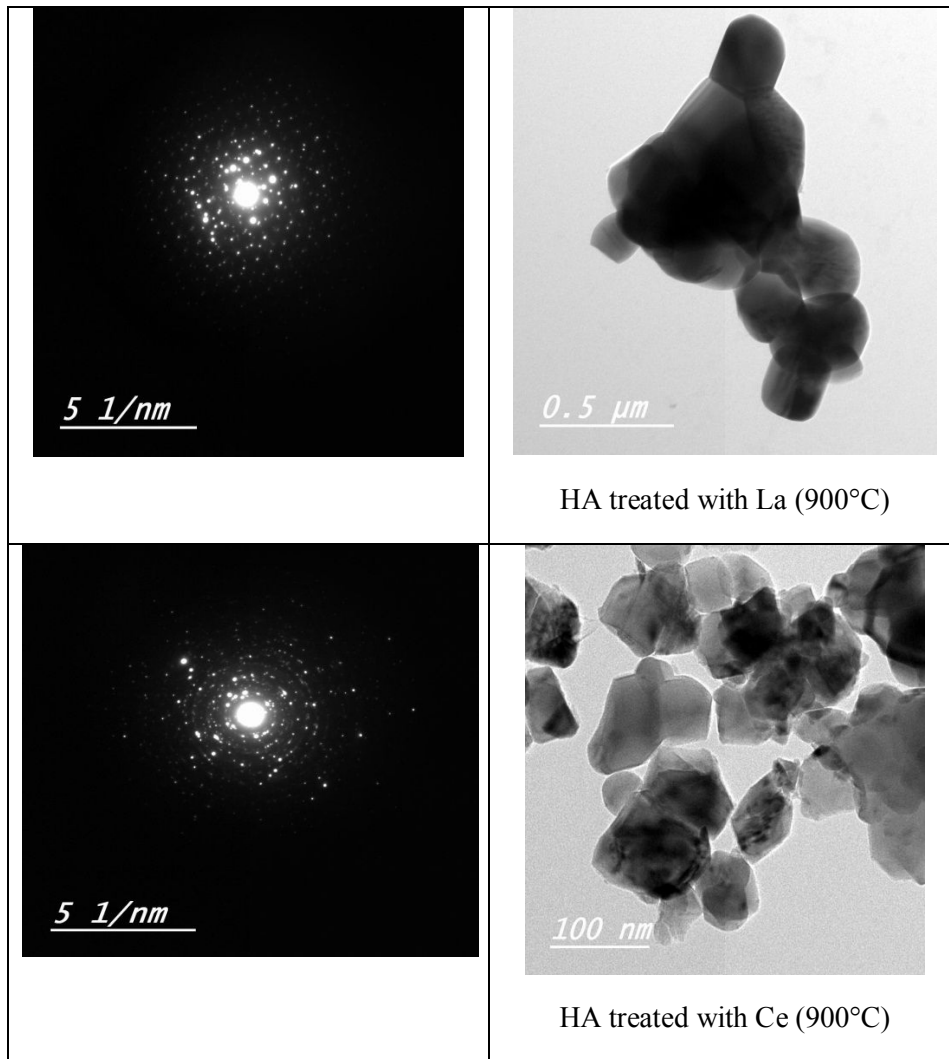


Fig.3. The TEM and the corresponding selected area diffraction patterns of the doped and undoped HAP samples (La or Ce =0.75 %) calcinated at 900 °C.

3.4. Infrared spectra of the hydroxyapatite and doped with La or Ce

Fig 4 represents the IR absorption of the seven prepared samples (pure and doped samples). IR curve of the prepared HAP is in agreement with the pattern of IR obtained in the previous work by the author⁽³⁾, also, ingreement with other curves obtained by other authors^(1,2).This finding confirmed the formation of the hydroxyapatite. The IR curves of the doped samples with La or Ce (0.25, 0.50, and 0.75 gm) behave the same trends as that recorded for the undoped HAP.

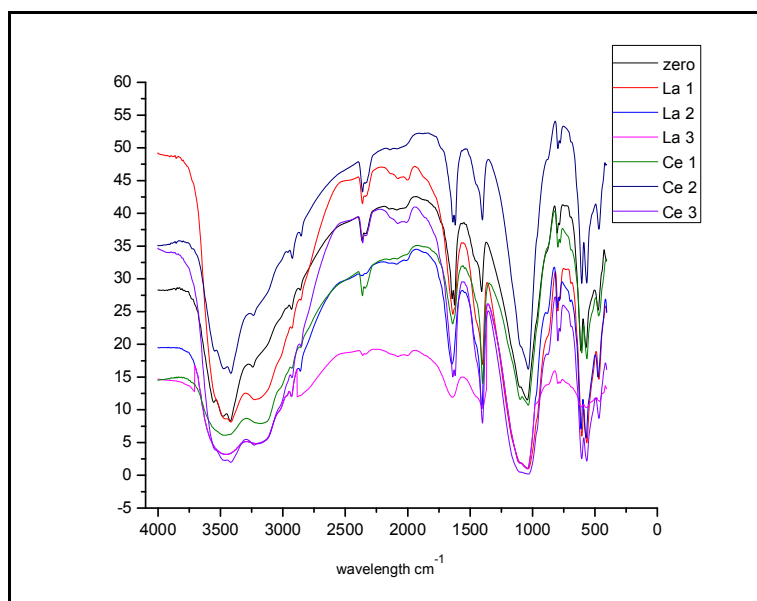


Fig. 4. IR spectra of the doped and undoped HAP samples (La or Ce =0.25, 0.5, 0.75 %)

For all samples different absorption peaks were observed and recorded in Table 1. A series of the absorption bands between 3300-3600 cm^{-1} were observed and attributed to OH and H_2O . The appearance of absorption band especially at 3600 cm^{-1} were associated to O-H stretching mode of the surface P-OH groups as that observed by⁽¹³⁾. The formation of this band may due to the partial protonation of the surface PO_4^{3-} ions to balance the cations deficiency of HAP^(13,14). A band corresponding to the H-O-H bonds of lattice water was observed at 2400 cm^{-1} . A series of bands appeared at 1097, 1100, 900, 600, 550 and 460 cm^{-1} specified the phosphate groups of the apatite unit were appeared in all samples. To explain this series of bands, the band at 1100 cm^{-1} may be attributed to the triply degenerated antisymmetric stretching of P-O bond while the appearance of the absorption band at 900 cm^{-1} can be attributed tonon-degenerated symmetric stretching of P-O band. In the same approach, the two bands appear at 600 and 550 cm^{-1} are associated with the triply degenerated vibration of O-P-O. The appearance of the C-O band at 1400 cm^{-1} was associated with the vibrational modes of carbonate ions means the substitution of some OH groups of the apatite by CO_3^{2-} during the preparation by oxidation⁽³⁾.

Table 1. IR spectra of the doped and undoped HAP samples (La or Ce =0.25, 0.5, 0.75%)

| Group cm^{-1} | Associated to |
|------------------------|--|
| 3300- 3600 | OH, H_2O |
| 2400 | H-O-H bonds of lattice water |
| 1600 | OH stretching mode |
| 1400 | the vibrational modes of carbonate groups |
| 1100 | ν_3 antisymmetric P-O |
| 900 | ν_1 non-degenerated symmetric stretching of P-O band |
| 550,600 | ν_4 vibration of O-P-O bond |
| 460 | O-P-O bond |

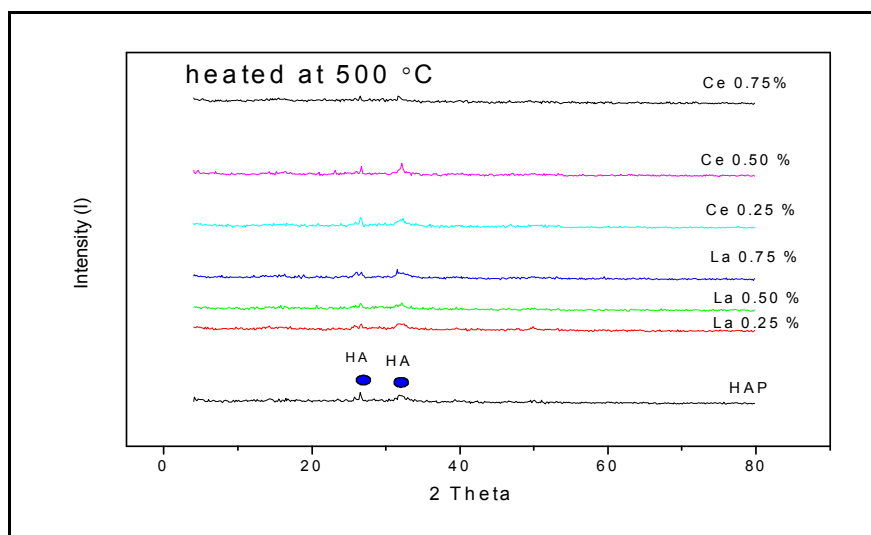
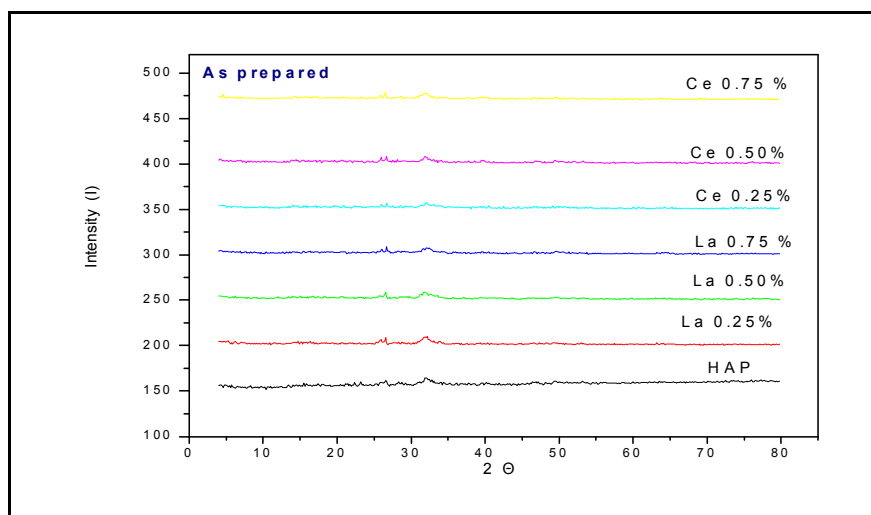
Table 2: comparison between cations in ionic radius and electronegativity

| Cations | Ionic radius | electronegativity |
|---------|--------------|-------------------|
| Ca | 1.0 | 1.0 |
| La | 1.032 | 1.1 |
| Ce | 1.07 | 1.1 |

Since the IR technique is used to study the covalent bonds only, it is unable to give direct evidence on the doping of Ca^{+3} by the La^{+3} or Ce^{+3} , so that no evidence on the IR chart was clarified. On other hand, where the rare earth cations have an electro negativities and ionic radii near the value for of Ca^{+3} , so the substitution can be occurred Table. 2

3.5. X-ray diffraction of hydroxyapatite and doped with La or Ce

X-ray diffraction of the as prepared samples was performed to study the composition and the structure of the produced phases, Fig 5a. Also, the doped samples with different percentage of La (0.25, 0.5, 0.75 gm) or with Ce (0.25, 0.5, 0.75 gm) were examined to study the effects of doping on the structure and the crystallinity. The x-ray patterns of the doped and the undoped samples show two small peaks at $2\Theta = 26.7$ and 32.48 which characteristic poor crystalline hydroxyapatite formation as matched with JCPDS 09-043 card of the pure hydroxyapatite. By doping with different percentage of La or Ce no changes were observed in the values of 2Θ or d. This produced phase corresponding the hexagonal system as indicated by different works⁽⁸⁾ and as shown by TEM phytos Fid.1. In this crystalline system, the unite of hydroxyapatite built up by three main groups, OH^- , Ca^{+2} , and PO_4^{3-} , The hydroxyl group arranged at the edges of the unit cell in the form of $-\text{OH}-\text{OH}-\text{OH}$ forming a like column structure, where the oxygen atoms spaced in a position prevent the hydrogen bond formation. Two types of calcium cations are included in the hexagonal unit (Ca I and Ca II), where Ca I , are located at the edges of the hexagonal unit cell and Ca II form equilateral triangles groups⁽¹⁵⁾. The phosphates ions are the main ions that build the unite cell which determine the structure of the hexagonal unit. From this structure building and the arrangement of the main groups through the building, HAP has a high capacity for substitution or exchanges. For examples OH^- groups may be substitute by smaller ions such as the halogen, PO_4^{3-} can be substituted by BO_3^{3-} or CO_3^{2-} and Ca could be substituted by some cations like the rare earth elements.



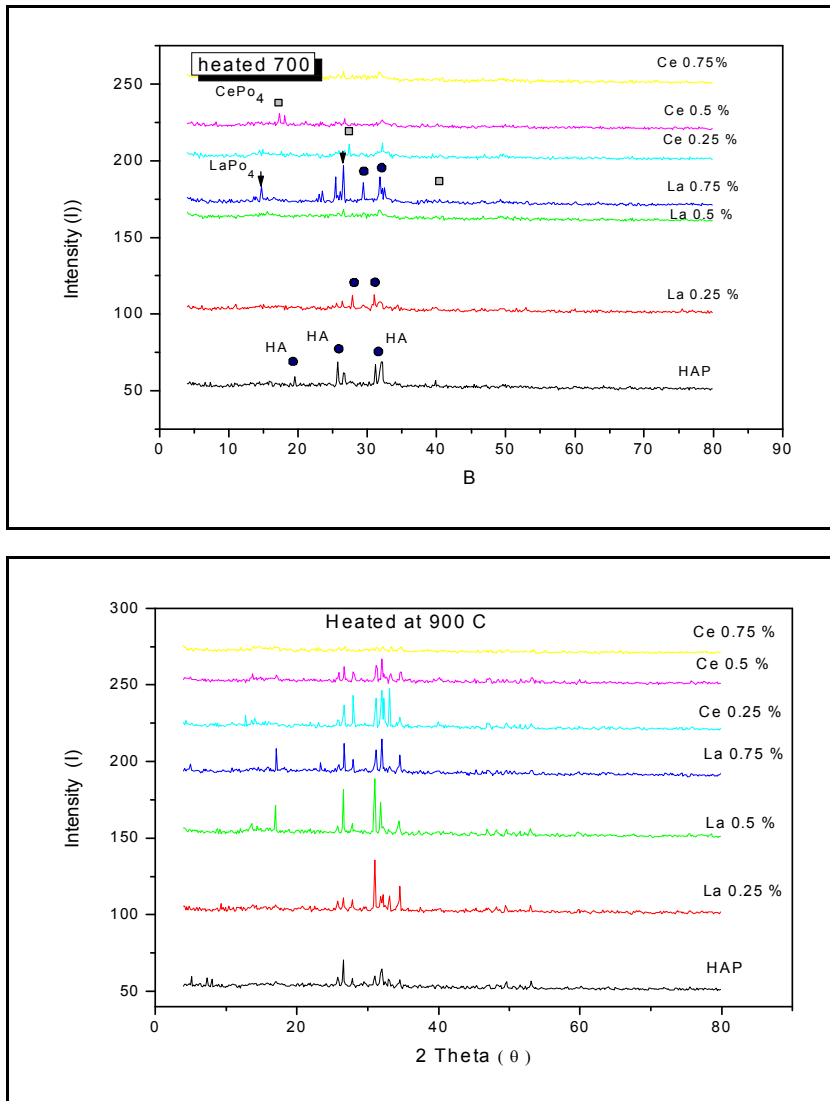


Fig 5. X-ray diffraction of the doped and undoped HAP samples (La or Ce =0.25, 0.5, 0.75 %)

Fig 5b,c,d represents the x-ray pattern of the doped and undoped samples at different calcination temperature, 500,700 and 900°C. For the undoped sample, the x-ray patterns show that when the sintering temperature increased up to 900 °C, there is an increase in the crystallinity of the samples, where the peaks of XRD patterns belonging to HAP becomes more narrow and the peaks intensities increases. In the case of the doping with La at different concentration, a specific peak appeared at $2\Theta = 14.72^\circ$ refer to the formation of LaPO₄ at 0.75% of La while in the case of Ce doping HAP with 0.5% a peak at $2\Theta = 18.08^\circ$ was appeared corresponding to formation of CePO₄. The formation of LaPO₄ or CePO₄ during the doping indicates that the La or Ce cations go partially to doped the HAP structure and the other parts goes to form LaPO₄ or CePO₄.

In all cases, the increase in the crystallinity by calcination may due to the recrystallization the HAP units by heat treatment.

3.6. Thermal Analysis of hydroxyapatite and doped with La or Ce

To study the thermal behavior and the thermal stability of the doped and undoped samples, the TG and the DTA were performed from the room temperature up to 1000 °C. The results of the thermogravimetric analysis were recorded in Fig 6. For the undoped samples, three steps were characterized on the TG profile. The first step starts at the room temperature and ending at ~100 °C corresponding to the liberation of absorbed water on the surface of the particles, while the second step corresponding to the crystallization of the particles starts at ~100 °C and ending at 460 °C. This observation is confirmed by the effects of calcination on the crystallinity of the formed phase, where the specific peaks on the XRD for the as prepared HAP becomes considerable by

calcination at 500 °C as shown in Fig 5. By further heat to 1000 °C, the weight loss is nearly negligible; this means that the formed HAP is thermally stable up to 1000 °C. The DTA curves of the as prepared HAP sample exhibit two main endothermic peaks 100 °C and 550°C at the temperatures corresponding to the water liberation and increase the crystallinity in agreement with the data obtained for the TG curves ⁽¹⁶⁾.

For the doped samples of HAP with 0.25,0.5,0.75 gm La or Ce, the same behavior including the two main steps for weight losses are observed but the second step which corresponding to the recrystallization shifts to higher temperature (620 °C). By following the increase of the La percentage, the same trends were observed and the temperature of the ending stages shifts to higher temperature. These results were confirmed by measuring DTA as shown in Fig 6. Both the TG and DTA profiles and the observation in the case of doping with La are obtained in the case of doping with Cocations with shifts the boundary of the thermogravimetric stages to higher temperature. From the analysis of the obtained data of TG and DTA, it may conclude that the doped with La or Cocations increase the thermal stability of the products

4. Conclusion

From the obtained results, it may conclude that phosphogypsum converted to hydroxy Apatite with nano-particle size. The morphology of the samples indicated that the hexagonal structure is the predominant crystals for the doped and the undoped samples. All the prepared samples are thermally stable up to 1000 C. The doping with La or Ce increases the thermal stability and improves the crystallinity.

5. Acknowledgement

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6. References

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