# Effect of Manganese Addition on Structure and Properties of Hydroxyapatite Synthesized from Eggshells

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## ABSTRACT

In this research, manganese added hydroxyapatite was synthesized from eggshells by precipitation method. Structure and properties of the samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR). The intensity of XRD pattern and crystallite size of hydroxyapatite decreased with increasing manganese concentration. Function groups of hydroxyapatite and manganese were confirmed by FTIR. The experimental results indicated that the manganese can be improved the properties of hydroxyapatite by precipitation method.

**Keywords:**Hydroxyapatite, Eggshells, Manganese, Precipitation method

## Introduction

The hard tissue of vertebrates is inorganic component as bone and dental enamel. The bone and enamel have calcium phosphate which is hydroxyapatite (HAp) phase [1]. HAp with chemical formula $Ca_{10}(PO_4)_6(OH)_2$has the capability to from chemical bonds with surrounding hard tissue. HAp has considered for applications such as bioceramics and born graft surgery [2]. Various techniques have development to prepare HAp and categorized into two techniques of preparation; solid state reaction and wet technique. Precipitate is one technique of wet technique. Precipitate technique due to better control composition and physical properties, low cost and easily to apply to industrial production [3]. HAp can be prepared from different natural materials such as bovine bone [4]. All the natural materials to preparation must be component of calcium. Egg shells have more 95% of calcium and waste from community. HAp from synthesis has poor properties than bone of vertebrates. The researchers have been to improve HAp properties with dope some elements such as Mg, Zn, Co, Cu, Cr, Mn, etc [5]. Mn is important element of bone structure and bone metabolism [6]. HAp was doped Mn that increasing the mechanical properties with increased Mn element [5]. In this research, HAp was synthesized from chicken egg shells and doped Mn element by precipitate technique. The structure and function groups of HAp were characterized with X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), respectively.

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## Materials and Methods

### Materials

Chicken egg shells were obtained from Charoen Pokphan Foods, (CPF) public company limited, Bangkok, Thailand. Diammonium hydrogen phosphate ($(NH_4)_3HPO_4$), ammonia solution, manganese dioxide ($MnO_2$) and nitric acid were perched from Sigma-Aldrich Company, USA.

### Preparation of samples

The membrane of egg shells were removed and washed with distills water to remove adhesion. The egg shells were dried in the air for a few days. The egg shells were grinded into powder with agate and mortar. Finally, the egg shells were heated at 1300 °C with rate 5 °C/min in room temperature.

The calcium oxide (CaO) powder from egg shells were mixed with $MnO_2$ powder at different percent weight from 1 to 9 with an increment 2%weight. The CaO and $MnO_2$ were mixed with $HNO_3$ and adjusted pH with ammonia solution. Then, it was precipitate with $(NH_4)_3HPO_4$ solution and ammonia was used to as agent for pH adjustment. The reaction of the formation is follows [7]:

$$(10\text{-}x)Ca^{2+} + xMn^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{(10-x)}Mn_x(PO_4)_6(OH)_2 \qquad (1)$$

The 800 ml of $(NH_4)_3HPO_4$ solution was dropped in the 700 ml of $CaO\text{-}MnO_2\text{-}HNO_3$ solution with vigorous stirring. The pH of solution was adjusted to 12 with ammonia solution. These experiments were synthesized in nitrogen atmospheric. The solution was kept at room temperature of 48 h and washed with distilled water until was not detected ammonia in solution. The sample was fileted with no.1 of filter paper (Whatman, UK) and kept in oven at 90 °C for 48 h.

### Samples characterization

The structure properties and homogeneous dispersion of the samples were investigated by X-ray diffraction (XRD) using Bruker D8 Advance diffractometer with $CuK_\alpha$ radiation generated at 30 kV and 30 mA. The samples were measured from 10° to 50° (2 Theta) with a step size of 0.02° and a count time of 1 s per step. The average crystallite sizes of samples werecalculated by the following equations [8]:

$$D=\frac{0.89\lambda}{\beta\cos\theta} \qquad (2)$$

Where D is the crystallite size, $\lambda$ is the wavelength of the X-ray radiation (1.5418Å),$\theta$ is the diffraction peak position of the sample, $\beta$is the full width at half-maximum intensity (FWHM).

FTIR spectra of the samples were measured at room temperature by Perkin Elmer (spectra two) spectrometer. The samples were measured within a range of 400 to 4000 $cm^{-1}$, 16 scans and spectral solution of 2 $cm^{-1}$.

## Results and Discussions

### Crystal structure

The X-ray diffraction patterns of chicken egg shell before and after heated at 1300 °C shown in Fig.1. The structure of chicken egg shells were identified as a calcium carbonate ($CaCO_3$) which according with JCPDS files no. 82-1690. At 1300 °C, the chicken egg shells were analyzed as calcium oxides (CaO) that corresponding with JCPDS file no. 48-1467. The results were indicated that the chicken egg shells were completely transformed to CaO at 1300 C.

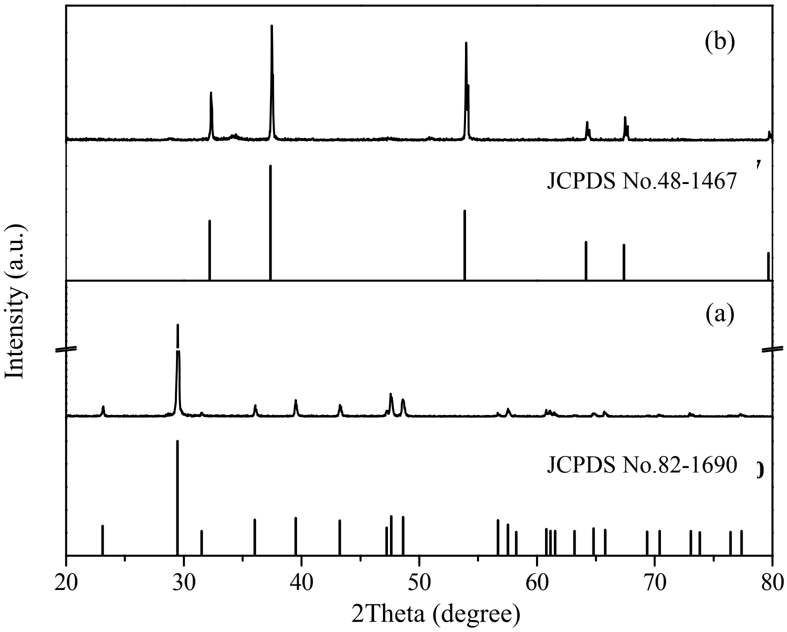

**Figure 1**The X-ray diffraction patterns of chicken egg shell (a) before and (b) after heated at 1300 °C.

Fig. 2 showed the X-ray diffraction patterns of products with various Mn concentrations. The major peaks of the raw material were appeared at $2\theta$ about 25.87, 31.77, 32.19, 32.90, 34.82, 46.71, 49.47, 50.49, 53.10, 51.29 and 53.15°, respectively as presented in Fig.2a. There is a no other crystalline species detect in raw materials powder. The XRD pattern of the raw materials was according with JCPDS file no. 09-0432 for calcium phosphate ($Ca_{10}(PO_4)_6(OH)_2$) that is hydroxyl apatite (HAp) phase. This was hexagonal system and space group P63/m. The XRD pattern of HAp added different Mnconcentration showed in Fig. 2b-f. The new peak of Mnconcentrationwere appeared at $2\theta$ about 28.83° which accorded XRD pattern of raw $MnO_2$. The intensity of XRD pattern of Mn was increasing with increased amount Mn as shown in Fig. 3. On the other hand, the intensities of HAp were decreased with increased amount of Mn as presented in Fig. 4. The crystallite size ($D_{211}$) of the HAp and ($D_{110}$) of Mn as shown in Fig. 5. The crystallite size of Hap was rapidly decreased as mount of HAp decreased (Fig. 5a) and crystallite size of Mn increasing with increased amount of Mn (Fig. 5b). These results corresponding with experiment of Torres, P., M., C. and et all [9]. The Mn was substituted for Ca sites in HAp structure and indicated the formation of Ca deficient HAp [10,11]

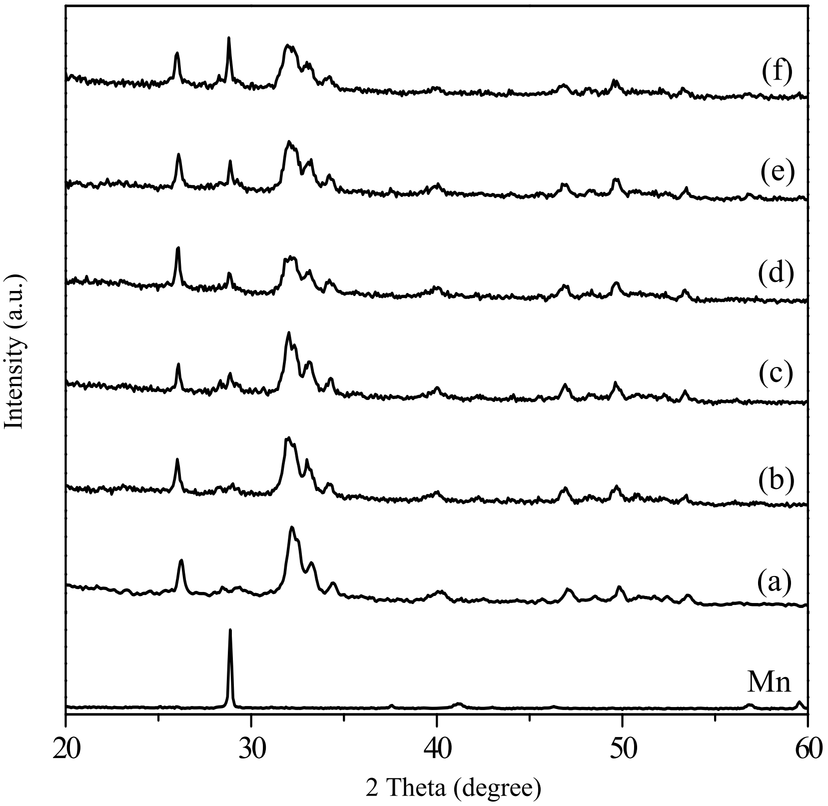

**Figure 2**The X-ray diffraction patterns of Hapdopped with Mn various concentrations (a) Hap (b) 1%Mn-HAp (c) 3%Mn-HAp (d) 5%Mn-HAp (e) 7%Mn-HAp and (f) 9%Mn-HAp

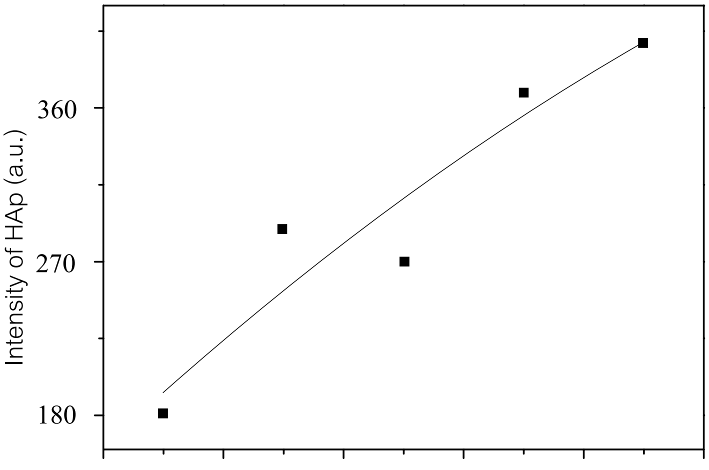

**Figure 3**The relationships between intensity of XRD and Mn concentration.

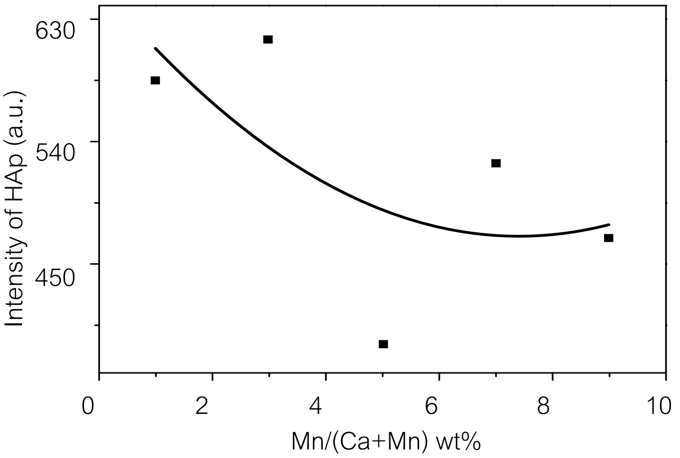

**Figure4**The intensity of XRD patterns of HAp as function of Mn concentration.

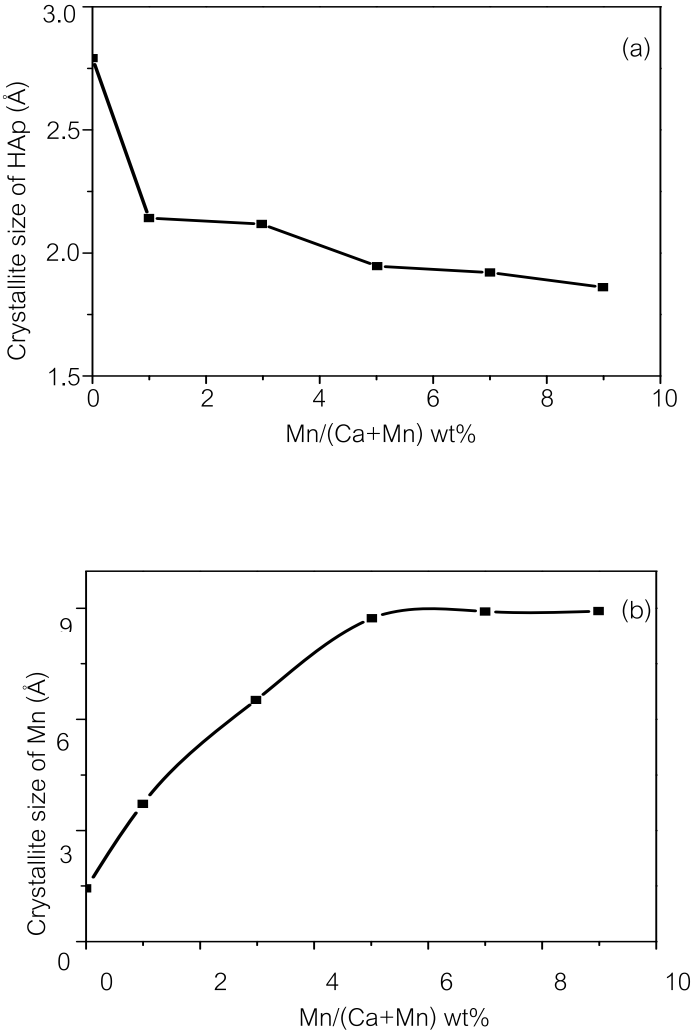

**Figure 5** Crystallite size of Mn-HAp as a function of Mn concentration (a) Mn (b) HAp.

Functional group

Fig. 6 shows the FTIR spectra of the HAp added Mn at different concentration. The FTIR spectra showed that the characteristic bands of HAp at 562, 604, 1022 and 1096 $cm^{-1}$ [12] as summarized in table 1. Transmittance band of $PO_4^{3-}$ was decreased with increasing amount of Mn as shown in Fig. 7. These the results indicated the crystallite size of HAp decreased with increasing Mn concentration and agreed with the XRD results.

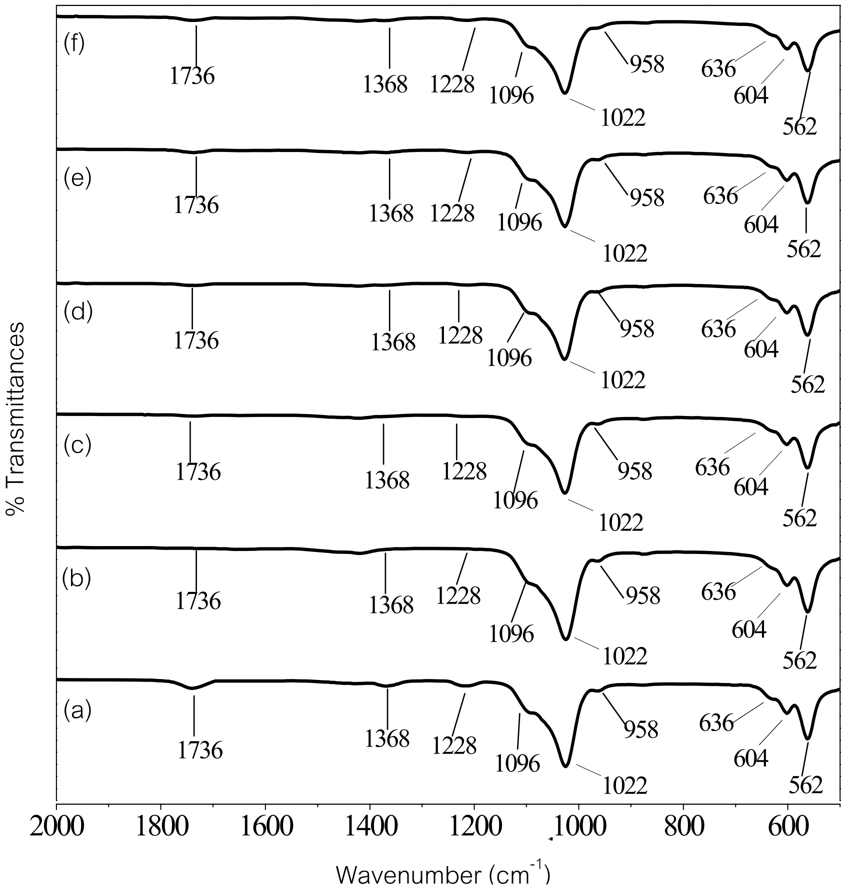

**Figure 6** The FTIR spectra of the HApdopedMnvarious concentration(a) HAp (b) 1%Mn-HAp (c) 3%Mn-HAp (d) 5%Mn-HAp (e) 7%Mn-HAp and (f) 9%Mn-HAp.

**Table 1**FTIR vibration modes of synthesized Mn-HAp [13].

| **Vibration line of characteristic groups** | **Vibration modes ν ($cm^{-1}$)** |
|---|---|
| $PO_4^{3-}\nu_4$ | 562 |
| $PO_4^{3-}\nu_4$ | 604 |
| OH | 636 |
| $CO_3^{2-}\nu_4$ | 958 |
| $PO_4^{3-}$ stretch $\nu_1$ | 1022 |
| $PO_4^{3-}\nu_3$ | 1096 |
| $CO_3^{2-}\nu_3$ | 1228 |
| $CO_3^{2-}\nu_3$ | 1368 |
| OH | 1736 |

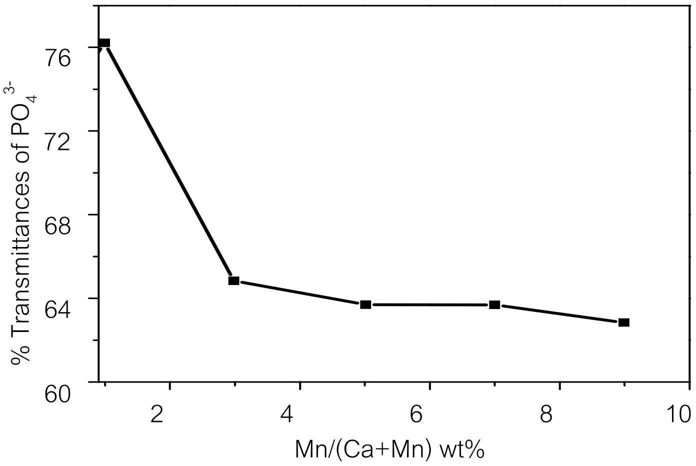

**Figure 7** The intensity of transmittance band of $PO_4^{3-}$ of HAp doped Mn various concentration.

## Conclusion

In this paper, $CaCO_3$ form chicken egg shells were transformed to completely CaO at 1300 °C and HAp can be synthesized from CaO from chicken egg shell. HAp doped with Mn was synthesized by precipitate method at different concentration of Mn. Crystallite size of Hap was changed in order of Mn concentration that increased with decreasing crystallite size. Mn was substituted for Ca site in HAp structure. This experiment shown that the Mn can be dope in HAp.

## Acknowledgement

The authors gratefully acknowledge the support given to this work by faculty of science, King Mougkut's University of Technology Thonburi. The authors would like to sincere thanks to department of physics, faculty of science, Kasetsart University provided tools for experiment.

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