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Co-Dopands on Hydroxyapatite in Structural, Morphology And in Antibacterial Activity

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Keywords: calcium phosphate, Mg/Zn chloride, FESEM, precipitate method.

ABSTRACT. Hydroxyapatite is calcium phosphate mineral substituted with Mg/Zn anion using precipitate method which indicates the changes in structure using X-ray diffraction. The functional groups of the material shows the bonds and morphology were analyzed using Field Emission Scanning Electron Microscopy. The application of ions doped in hydroxyapatite, which gives antibacterial activity for improving medical application due to its biocompatibility.

Introduction. Material with more stable with high dense which is insoluble in Calcium Phosphates is Hydroxyapatite (Hap) in two crystal forms Monoclinic and Hexagonal. In practical hexagonal is important because monoclinic form is destable with small amount of foreign ions. Ionic substitution used to improve the biological performance of calcium phosphates developing the applications in biomedical field [1]. The ions Zn, Cu, Sr provide crystallinity also it increase antimicrobial, Ag-Zn ions substituted using microwave refluxing method used for biomedical applications [2]. Ag has higher Antibacterial activity with less toxicity but it is limited due to its high cost and discoloration. A Zn ion has antibacterial activity with less toxicity with color stability, heat resistance in low cost. Hap substituted with single and also as co-do pants investigating photo luminous using Mn with Sb and compatibility, corrosion resistance using Zn doped Si, Ag improves mechanical and biological behaviour of Hap by substituting Zn with F'Ti incorporate in Ag with Hap provides bioactivity and bio compatibility as nanotubes using for implantations. TiO₂ doped Ag has potential application on photo catalysts, oxidation on gas sensors, cell membranes, toxic contamination on water to CO₂ [3-8]. Co-do pants varying different anions affects structure and morphology of Hap. Mg, Zn ions are trace elements present in human body due to properties (ie. formation of bones) using Sol-gel method with high purity. The Mg ion increases the solubility and reduces the lattice parameters improves crystallinity by increasing Mg ratio and Zn ion gives changes in morphology, increase stability to materials which reduces thermal stability. Morphology may be irregular form agglomeration by increasing Zn content. Ions with less ionic radius, which give stability to the Hap and increase the solubility with decrease in lattice parameters. Ceramic materials with different anions used for surface modification to improve both mechanical and corrosion property for implantation. Zn acetate added with Hap, which improves antibacterial activity using extraction method, provides oral hygiene products. Ag with Zn oxides using plant extract which increase the antibacterial activity and also it kills the cancer cells [9]. Ions Ag-Zn nitrates on Hap determines their benefit on biomedical applications. Previous studies focused on individual substitution of ions in Hap also with co-do pants but varying different anions not yet reported based on the medical applications. Ionic substitution improves properties of hydroxyapatite.

Various methods are used for synthesizing Hap such as sol-gel method [10], hydrothermal method [11-12], micro wave irradiation [13-14], electro deposition method [15], precipitate method [16-
17]. Wet precipitate method were used in order to avoid carbonate into mg doped Hap. In addition, the product up to 5.7% was similar to biological apatite without toxicity. As mentioned above there are various reports on ion substituted Hap but differing anions on hap substituted were rare. The paper focused on hydroxyapatite substituted with Mg/Zn chloride, which enhance property of Hap and used in various applications such as in implantation, anti-bacterial activity, sensors. The Zn is the bioactive material increase bioactivity and used as an antimicrobial activity.

**Material and Methods.** Calcium nitrate tetra hydrate (Ca(NO$_3$)$_2$.4H$_2$O) Mw 236.15 with Di-ammonium hydrogen phosphate (NH$_4$)$_2$HPO$_4$, Mw 132.06, Ammonium hydroxide (NH$_4$OH), Magnesium Chloride hexa hydrate (MgCl$_2$.6H$_2$O), Zinc chloride (Zn Cl$_2$. H$_2$O), Mw 136.29.

**Preparation of Hydroxyapatite.** Calcium nitrate tetra hydrate dissolve in 50 ml of Millipore water and Di-ammonium hydrogen phosphate dissolved in 50 ml of water. (NH$_4$)$_2$HPO$_4$ added drop wise to (Ca(NO$_3$)$_2$.4H$_2$O) maintain pH at 9 using NH$_4$OH. The obtained precipitate washed with distilled water several times and dried at 80°C (Ca / P) grinded using mortar pestle for different characterizations. The Mg/Zn chloride was doped using same procedure in Calcium nitrate (Ca+ X)/P (X-Mg/Zn chloride) as in given Table 1.

**Table 1. Elemental Composition of Samples.**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>CN</th>
<th>NHP</th>
<th>MZN</th>
<th>MZC</th>
<th>MZCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NHP</td>
<td>-</td>
<td>0.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MZCL</td>
<td>0.98</td>
<td>0.67</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>CL6</td>
<td>0.96</td>
<td>0.67</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Result and Discussions.** The addition of dopands into Hap gives structural changes, crystal linty. XRD shows broad peaks which indicate amorphous material forms nano-size particles (Fig. 1). The JCPDS (09-0432) for hydroxyapatite shows sharp peaks as well crystallinity and doping Chloride ions shows just increase in intensity (i.e. broad peaks) with decrease in lattice parameter may be due to smaller ions incorporate into Hap. The Mg in Ca II site which decrease c-axis, which shows decrease in crystallinity used in various applications such as coatings to carry drugs and also improved bone induction. The increase in a and decrease in c due to the Cl ion as reported in paper [18]. The changes in lattice parameter and in volume due to the anions which showing that chloride increases a and decrease in c [18]. And also volume shows decrease for the components and hkl value of the peaks 002, 211, 310, 222 were shown in XRD analysis with 2-theta values mentioned in Table 2.
Table 2. Lattice parameters and volume.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ value</th>
<th>Unit cell parameters</th>
<th>Volume(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAP(09-0432)</td>
<td>-</td>
<td>a c</td>
<td></td>
</tr>
<tr>
<td>Hap</td>
<td>31.77</td>
<td>9.418 6.884</td>
<td>528.80</td>
</tr>
<tr>
<td>CL</td>
<td>31.87</td>
<td>9.415 6.886</td>
<td>528.61</td>
</tr>
<tr>
<td>CL6</td>
<td>9.412</td>
<td>6.887</td>
<td>528.56</td>
</tr>
</tbody>
</table>

**FTIR.** In this FTIR analysis (Fig. 2) which shows the functional group of the material, the value 500-560 indicates vibration mode of PO₄³⁻, value between 565-570 shows bending mode of PO₄³⁻ and between 1000-1040 shows stretching mode of PO₄³⁻. Assymetric stretching of PO₄³⁻ between 1030-1120 and values at 1650-1065 indicates OH deformation and 632-634 and in 3500 indicates OH vibration mode.

**FESEM.** FESEM gives the morphology of the samples in nm range gives particle size 50-70 nm and for MZCL 44-64 nm. The agglomeration with small elongation in spherical shape may due to Zn ion in Hap [3]. No morphology changes by decreasing the dopants concentration as shown in Fig 3.
Fig. 2. FTIR Spectra.

Fig. 3. FESEM for pure Hap and doped Hap with (0.01 & 0.02) concentration.

**Antibacterial Activity.** The antibacterial activity test analyzed by well diffusion method using Mueller Hinton agar using 100ml of water and sterilized poured into petriplates and solidification
using the pathogenic bacterial strains _E. Coli_ and _S. aureas_. The plates were kept at hot air oven in 37° C for 24 hours incubation. The plates were read after 24 hours which shows that pure Hap does not exhibit but doped with Mg/Zn chloride exhibit 18-24 mm in _E.coli_ and in _S.aureas_ form 15-20 mm (Fig. 4).

**Fig. 4. Antibacterial activity for a) pure Hap and doped Hap b) s.aureas and c) E.coli.**

The results occur due to the metal ions interaction with proteins or interaction with antibacterial membranes causes structural change and porousness.

**Summary.** In this present work co-dopands Mg/Zn chloride with hydroxyapatite gives the structural changes which confirmed by XRD and functional groups of different vibration modes were shown in FTIR. The morphology changes with spherical elongation gives through FESEM and antibacterial exhibit 18-24 mm in _E.Coli_ and 15-20 mm in _S.aureaus_, which can used in various applications.

**References**


[2] C. Ning, X. Wang, L. Li, Y. Zhu, M. Li, P. Yu, Y. Zhang (2015), Concentration ranges of antibacterial cations for showing the highest antibacterial efficacy but the least cytotoxicity against mammalian cells: implications for a new antibacterial mechanism, Chemical research intoxicology, 28 (9), 1815-1822, DOI: 10.1021/acs.chemrestox.5b00258.


