The Dielectric Study of Calcium Hydroxyl Apatite Doped By Magnesium Ions

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Hydroxyapatite is considered as one of the most effective biomaterials with general formula Ca_{10} (PO_4)_6 (OH)_2. Many substances have been used for doping hydroxyapatite like F, Mg, CO_3, Zn, Bi and Na, to improve the properties of the HA crystal. In this paper, we discuss the influence of magnesium ions on the electrical properties of the HA crystal. Pure HA (S1) and Mg loaded hydroxyapatite (S2, S3 and S4) of different magnesium concentrations have been prepared by wet precipitation method. The dielectric parameters ε′ and ε″ measured at different temperatures and relaxation times of relaxation process was calculated from the Cole-Cole plot. The advantages of modulus studies were to recognize the conduction process and study the effect on the frequency and estimate the relaxation frequency. Conduction mechanism has been studied using alternating current measurements, analyzing their dependence on temperature and frequency. The exponent (S) was estimated to recognize the type of conduction. The activation energy studied also to confirm the conductivity measurements. The electrical measurements confirmed that as the addition of Mg increased, the conductivity of the substance would increase and this will improve the bioactivity of HA.

Keywords: Hydroxyapatite, Magnesium, conductivity.

Introduction

Hydroxyapatite, Ca_{10} (PO_4)_6 (OH)_2, HA, one of the most famous biomaterials owing to its similarity with bone and teeth composition, therefore it can bond to bones without any infection and fibrous encapsulation, and this knowing as bioactive and biocompatible [1]. However, its application is limited cause of its brittleness. One solution is to substitute the HA constituents by some other metal to improve its chemical properties. Therefore the bioactivity and biocompatibility are utilized along with the good mechanical properties of the metal [2].

Hydroxyapatite directly attach to the living tissues through formation of calcium carbonate apatite layer, leading to interfacial bonding [3-4]. HA is used in other application areas, which are based on electrical behavior of HA, such as chemical sensor [5-6], ion-exchanger [7-8], fuel cell [9]. It also used for electrical applications such as an electrical insulating coating for electronic devices including dielectric coating and implantable devices [10]. It is know that the electrical and dielectric properties are useful for biomaterial applications since the bone is natural composite made up of fluids, collagen and HA matrix [11].

In the HA structure, there is a lattice of hydroxide ions located at the centre of Ca^2+ triangles along the c-axis of a hexagonal unit cell [12]. The OH ions are aligned in columns parallel to the c-axis, along with Ca^2+ and (PO_4)^3− ions [13]. Since the hydroxyl ions within the c axis columns are thought to have an important role in ionic conduction [12], HA has been regarded as a one dimensional anionic conductor. The influence of porosity on the room temperature permittivity of HA reported to understand its interaction with electrical fields applied to improve fracture healing or enhance bone growth [14-15]. Hence
it is necessary to study the electric and dielectric properties of HA to have better understanding of electrical and biological phenomena.

**Aim of paper**

The present paper deals with measurements of electrical properties of HA and Mg-HA in detail. Hydroxyl apatite prepared by wet precipitation method and doped with different concentrations of magnesium ions the samples then characterized by XRD, FTIR, SEM and EDX, as described in previous work [16]. The electrical properties of the HA samples are studied in the frequency range of 0.01 Hz to 10 MHz. The temperature dependence on the electrical conductivity and dielectric loss of HAP against frequency were also studied. Finally activation energy and relaxation time estimated.

**Materials and Methods**

**Preparation of HAP nanoparticles**

For the preparation of control hydroxyl apatite sample, Di-ammonium hydrogen orthophosphate \((\text{NH}_4)_2\text{HPO}_4\) solution is dropped to Calcium Chloride dihydrate \([\text{CaCl}_2.2\text{H}_2\text{O}]\) solution to achieve necessary Ca/P molar ratio (1.67), which mimics the ratio of the Ca/P of natural bone. The precipitation reaction is carried out at 100°C temperature under vigorous stirring for five hours and during the process pH of the reaction is con rolled at 10 by using ammonia solution. The precipitate is aged for 24 hours at room temperature followed by rinsing with distilled water for the removal of ammonia. The product is then dried in an oven at 100°C and crushed into powder form. Magnesium Nitrate hex hydrate \(\text{Mg(NO}_3)_2.6\text{H}_2\text{O}\) add to \([\text{CaCl}_2.2\text{H}_2\text{O}]\) solution to prepare the Mg-HA samples

**The theoretical basis of the dielectric measurements**

The dielectric measurements were performed between 0.01 Hz and 10 MHz using a Novo control High Resolution Alpha Analyzer. Quatro Temperature Controllers using pure nitrogen as heating agent and assuring the temperature stability better than 0.2 K assisted the analyzer .The measurements were conducted, using gold plated stainless steel electrodes of 20 mm in diameter, in parallel plate capacitor configuration.

The high precision analyzer that operates over a broad frequency range. Temperature control unit enables molecular relaxation, conductivity, phase separation/transition, activation energy, rate of blending, aging, curing, and other studies. The frequency dependence of the A.C conductivity was given by the relation:[17-18]

\[
\sigma_{\text{ac}}(\omega) = \sigma_{\text{dc}} + \sigma_{\text{ac}}(\omega)
\]

\[
\sigma_{\text{ac}}(\omega) = A \omega^s
\]

and in the logarithmic form:

\[
h \sigma_{\text{ac}}(\omega) = h A + s h \omega
\]

Where, \(A\) is temperature dependence parameters, and the exponent \((S)\) is the frequency exponent factor and they could be obtained from the experimental curves. The total conductivity of a sample measured in the dielectric cell can be given by this relation [19]:

\[
\sigma_t = \sigma_0 + A \omega_p^S
\]

where \(\sigma_0\) is the D.C. conductivity component ( S. m\(^{-1}\) ), \(A\) and \(S\) are temperature – dependent factors and \(\omega_p\) is the angular frequency at which the charged ions diffuse to the other side of a living cell membrane .The critical frequency \(\omega_p\) which is defined as the hopping rate , that is .

\[
\omega_p = (\sigma_0 / 2A)^{1/S}
\]

The relation between \(\ln \omega_p\) ( sec\(^{-1}\) ) and \(1/T\) ( K\(^{-1}\) ) has been shown to be linear with in the observation temperatures and frequency ranges, thus we can assume that \(\omega_p\) is given by a simple Arrhenius formula:

\[
\omega_p = \omega_{0p} \text{Exp} (-E_a/ KT)
\]

where \(E_a\) is the activation energy ( ev ) due to temperature increase T ( K ) , \(\omega_{0p}\) is the initial frequency of the polaron ( Hz ), and K is the poltzman’s constant ( \(5.67 \times 10^8\) W. m\(^2\).K\(^{-2}\)). The \(E_a\) can be calculated from the slope of \(\ln (\omega_p)\) versus 1000/T.

The Cole-Cole analysis used to obtain the relaxation time of relaxation process. The average relaxation time \(\langle \tau \rangle\) calculated from equation:

\[
\langle \tau \rangle = \frac{\tau}{\nu}
\]

Where \(\nu\) is the distance on the Cole-Cole plot between \(\varepsilon_{\infty}\) and an experimental point, and \(u\) is the distance between the experimental point and \(\varepsilon_{\infty}\).
From the Cole-Cole plot the molecular relaxation time $\tau$ is evaluated from equation:

$$\varepsilon_0 \left[ \frac{\varepsilon_s^3}{\varepsilon_s^2 + \varepsilon_r^2} \right] =$$

Where $\varepsilon_0$ and $\varepsilon_s$ are the infinite frequency and static dielectric constants, respectively, $\varepsilon_r$ is the relaxation time.

Modulus equation:
Where $M'$ and $M''$ are the real and imaginary parts of modulus.

Results and Discussion

The dielectric parameters:

Fig [1] represent the relation between $\varepsilon'$ and $\varepsilon''$ with frequency at temperature (248, 273, and 298 K) respectively for sample of hydroxyl apatite control. The behavior of this curve appear that the increases in temperature was accumulation with shifted of $\varepsilon'$ and $\varepsilon''$ towards high frequency.

The trend is equally similar, where it rise sharply toward low frequency and decays at increasing frequency. It can be attributed to the electrode polarization effect which accumulation decrease relate with decreasing of both dielectric constant and dielectric loss. This is due to the periodic reversal of the electric field occurs so fast at high frequencies because there was no excess ion diffusion in the direction of the field [20].

In order to analyze the dielectric relaxation mechanism of the samples, we plotted the curves of $\varepsilon''$ vs. $\varepsilon'$, as shown in Fig. 2. It indicates the circles and the position, while diameter of the circles changes with Mg content and this confirms the incorporation of Mg into the HA structure.

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*Fig. 1. Shows the relation between the dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) respectively with the frequency for the hydroxyapatite crystal control at temperature (248, 273, and 298 K).*
Fig. 2. Cole-Cole plots HA control (S1) and Mg doped hydroxyl apatite (S2, S3 and S4) of magnesium concentrations [0.004, 0.01, 0.02 mole] respectively, at T = 298 K.
TABLE 1. The values of average relaxation time $\tau_0$ and the molecular relaxation time $\tau$ for HA control (S1) and Mg doped hydroxyl apatite (S2, S3 and S4) of magnesium concentrations [0.004, 0.01, 0.02 mole] respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_0 \text{ sec}$</th>
<th>$\tau \text{ sec}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>$7 \times 10^4$</td>
<td>$5 \times 10^4$</td>
</tr>
<tr>
<td>S2</td>
<td>$8 \times 10^4$</td>
<td>$4 \times 10^4$</td>
</tr>
<tr>
<td>S3</td>
<td>$9 \times 10^4$</td>
<td>$6 \times 10^4$</td>
</tr>
<tr>
<td>S4</td>
<td>$7 \times 10^4$</td>
<td>$5 \times 10^4$</td>
</tr>
</tbody>
</table>

The values of $\tau$ for (S1, S2, S3 and S4) are listed in Table 1, the obtained $\tau$ values of the Mg-substituted HA samples were slightly lower than the pure HA. As appeared in the XRD analysis, the phase composition of the samples is affected by the amount of Mg. The dielectric properties of the samples are also changed with the addition of Mg. Hence, the phase composition of the samples influences the dielectric properties such as the dielectric loss [21]. The percent of HA phase affects the permittivity and in turn the conductivity increased.

**Modulus Studies:**

The purpose of modulus (M) studies is to support the electrical conductivity data. The advantages of modulus studies were to recognize the conduction process and the effect on the frequency. Fig. 3, shows the frequency dependence of the real part of dielectric modulus $M'$ and imaginary part of dielectric modulus $M''$ respectively. From the graph, $M'$ and $M''$ increase towards high frequency. The increase of electrical modulus can be related to the conductivity, where at the higher frequency shows that conductivity arises. As showed in Fig. 4 where the presence of Mg in samples (S2 and S3) showed increasing in the electrical conductivity except for (S4) of Mg concentration, 1.5% the conductivity reduced again, this reduction may be due to the collisions happened between the extra Mg electrons. Therefore, it is recommended to exclude the Mg concentration of 1.5%.

As showed in Table 2, the relaxation frequency increased with increasing the Mg concentrations which indicating that the conductivity increased also with increasing the Mg concentrations.

![Fig. 3. The frequency dependence of the real part of dielectric modulus $M'$ (and imaginary part of dielectric modulus $M''$) respectively for pure HA sample and HA doped with different concentrations of Mg at $T=298K$.](image)
Fig. 4. Relation between the frequency dependence on the conductivity for HA control (S1) and Mg doped hydroxyl apatite (S2, S3 and S4) of magnesium concentrations \([0.004,0.01,0.02\) mole] respectively, at \(T= 298\) K.

TABLE 2. Represent the measurement values of relaxation frequency \(F_0\) for control (S1) and different Mg concentrations doped with HA (S2, S3 and S4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(F_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>(6.22\times10^4)</td>
</tr>
<tr>
<td>S2</td>
<td>(2.31\times10^5)</td>
</tr>
<tr>
<td>S3</td>
<td>(3.1\times10^6)</td>
</tr>
<tr>
<td>S4</td>
<td>(1.68\times10^6)</td>
</tr>
</tbody>
</table>

The distribution of relaxation peaks is due to the distribution of relaxation time of the free charge [22]. The existence of relaxation peak in real part modulus \((M')\) formation of higher frequency indicating the apatite electrolytes films are ionic conductor[23].

The contribution of electrode polarization phenomena can be ignored at lower frequency of \(M'\) and \(M''\). Furthermore, the tail was observed in lower part of frequency which indicates the samples are capacitive in nature for \(M'\) and the distribution of relaxation time of the ionic conductor for \(M''\) [24]. The existence of the long tail can be considered as the result of the large capacitance associated with the electrode[25].

**Conductivity Measurement**

The frequency dependence of conductivity \((\sigma)\) presented in Table[4-9] and it is represent in Fig.5 for all prepared samples at different temperatures. It noticed that the conductivity increased with increasing temperature and they show a typical ionic conductivity behavior of apatite due to the hopping and vibrational mode of the ions [26-27].

The increase in conductivity with the frequency is attributed to the relaxation of the mobile ion hopping. This suggests that the AC conductivity is obeys “Correlated Barrier Hopping” (CBH) mechanism [28].

From all curves in Fig.5, the exponent \((S)\) was estimated from the slope of each curve. All samples exhibit common behavior and it was found that, the exponent \((S)\) decreases with increasing temperature as shown in Table[3].

It was found in terms of electrical conductivity that the conduction mechanism depends on the apatite composition. Therefore, the non-stoichiometry of hydroxyapatite can influence the proton conduction.[29]

Fig.6 deduce from the relation of \((\ln \omega_p, vs 1000/T)\) for S1, S2, S3 and S4. The activation energy was estimated from the slope of the straight line relation for each sample at temperatures \((T= 248K, T=273K\) and \(T=298\) K).

As it showed in Table[4], it was observed upon the addition of Mg, that the activation energy decreased and this is in agreement with the conductivity increased with increasing the concentration of Magnesium. As it noticed

TABLE 3. The values of the exponent \((S)\) depends on the temperature for HA control (S1) and Mg doped hydroxyl apatite (S2, S3 and S4).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Exponent ((S))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>248K</td>
</tr>
<tr>
<td>S1</td>
<td>0.38</td>
</tr>
<tr>
<td>S2</td>
<td>0.25</td>
</tr>
<tr>
<td>S3</td>
<td>0.25</td>
</tr>
<tr>
<td>S4</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Fig. 5: The frequency dependence of the conductivity is shown in for HA control (S1) and Mg doped hydroxyl apatite (S2, S3 and S4) of magnesium concentrations [0.004, 0.01, 0.02 mole] respectively.
from XRD analysis that the crystallinity of HA decreased as Mg concentrations increased.

The poorly crystalline samples due to the presence of an appreciable amount of vitreous state, which facilitates ionic mobility [30], such as the presence of Mg, (HPO$_4$)$_2^-$ and carbonate contents, in the crystal of apatite. These additives increased the electrical conductivity with increasing the temperature. The obtained values of activation energy allow assuring that the dominant conduction mechanism is ionic. It is observed that the hydroxyl groups (OH$^-$) are the conducting species and the main charge carrier was (OH$^-$) (protonic conduction).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{\epsilon\omega\ln}$</th>
<th>$E_{\epsilon\omega\ln}$</th>
<th>$E_{\epsilon\omega\ln}$</th>
<th>$E_{\epsilon\omega\ln}$</th>
<th>$E_{\epsilon\omega\ln}$</th>
<th>$E_{\epsilon\omega\ln}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>6.00E+08</td>
<td>3.00E+08</td>
<td>6.00E+07</td>
<td>2.00E+07</td>
<td>5.00E+06</td>
<td>8.00E+05</td>
</tr>
<tr>
<td>S2</td>
<td>1.20E+09</td>
<td>5.00E+08</td>
<td>3.20E+08</td>
<td>6.00E+07</td>
<td>3.00E+07</td>
<td>1.00E+07</td>
</tr>
<tr>
<td>S3</td>
<td>8.00E+09</td>
<td>3.70E+09</td>
<td>2.50E+09</td>
<td>1.00E+09</td>
<td>6.00E+08</td>
<td>2.00E+08</td>
</tr>
<tr>
<td>S4</td>
<td>1.3E+10</td>
<td>1.0E+10</td>
<td>6.20E+09</td>
<td>1.50E+09</td>
<td>6.00E+08</td>
<td>5.7E+8</td>
</tr>
</tbody>
</table>

**Conclusion**

Hydroxyl apatite doped by different concentrations of magnesium prepared by wet precipitation method. The influence of magnesium on the electrical properties of the hydroxyapatite crystal was studied. As the Mg concentrations increased the dielectric constant $\epsilon'$ and dielectric loss $\epsilon''$ shifted towards low frequency indicated that Mg sharing with a type of electronic conduction, except for S4 which shifted towards high frequency. The behavior of S4 may be due to increase the number of electrons which may increases the collisions resulted in reducing the conductivity.
The obtained molecular relaxation time $\tau$ values of the Mg-substituted HA samples were slightly lower than the pure HA.

The real part ($M$) and imaginary part ($M'$) of dielectric modulus increase towards high frequency. The increase of electrical modulus can be related to the conductivity, where at the higher frequency shows that conductivity arises. The conductivity of HA and Mg doped HA increases with temperature following the Arrhenius behaviour. The activation energy for this system was reverse to the conductivity. The conductivity behaviour proved the HA is an ionic conductor. The conduction mechanism was found to follow the CBH model as exponent S decrease with increasing temperature.

References


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دراسة خواص العزل الكهربائي للكالسيوم هيدروكسيل الأباتيت مطعم بواسطة أيونات المغنيسيوم

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تعتبر الهيدروكسي أباتيت من أكثر المواد الحيوية فعالية والتي له الصيغة الكيميائية العامة Ca10[PO4]6(OH)2. وقد تم استخدام العديد من المواد لتطعيمه واستبدال الكالسيوم بعناصر أخرى مثل Bi، Zn، CO3، Mg، F، وقف تحسين خصائص بلوره الهيدروكسي أباتيت. في هذا البحث تم تأثير تطعيم الهيدروكسي أباتيت بآيونات المغنيسيوم على الخواص الكهربائية للبلورة. تم تحضير أربعة عينات: عينة النتائج الأولي هي الهيدروكسي أباتيت النقلي الخالي من أي تطعيمات وثلاث عينات أخرى تم إضافة تركيزات مختلفة من المغنيسيوم بلورات الهيدروكسي أباتيت. تم إضافة تركيزات مختلفة من المغنيسيوم بطريقة الترسيب. تم حساب ثوابت العزل الحقيقي وفي درجة حرارة مختلفة، وحساب وقت الاسترخاء من عملية الاسترخاء من طريقة كول كول. كانت نماذج دراسات المعامل هي التعرف على عملية التوصيل ودراسة التأثير على التردد وتقدير تردد الاسترخاء. تم دراسة التوصيل باستخدام قياسات التيار المتردد، تحليل اعتمادها على درجة الحرارة والتردد. تم تقدر الأس (S) للتردد على نوع التوصيل. تم دراسة طاقة التنشيط أيضًا لتاكيد قياسات الموصلية. أكدت القياسات الكهربائية أنه كلما زادت إضافة المغنيسيوم، فإن موصلية المادة ستزيد وهذا سيساعد النشاط الحيوي للهيدروكسي أباتيت.