THEORETICAL STUDIES OF SOLID STATE DIELECTRIC PARAMETERS OF HYDROXYAPATITE

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Abstract. This paper deals with the theoretical study on the density of the hydroxyapatite (HAp). The solid state dielectric properties such as valence electron, plasma energy, Penn gap and Fermi energy were also evaluated for the HAp using the empirical relation. These estimated values were utilized to report the electronic polarizability and dielectric susceptibility of the HAp.

1. Introduction

Recent research has found enhanced bone osteobonding and new bone growth on polarized hydroxyapatite due to the generation of a permanent surface charge [1-4]. The surface charge is not due to dipole rotation, as in ferroelectric materials, but is thought to develop from proton migration in the columnar OH^- structure of hydroxyapatite under an applied electric field at elevated temperatures [2]. It has been shown that bone growth is accelerated on the negatively charged surface of polarized hydroxyapatite and decelerated on the positive surface [1, 3] The mechanism is not clear, but rapid bone formation on negative surfaces is possibly due to adsorption of Ca^{2+} ions, which act as nuclei for calcium phosphate formation. The study of the electrical properties of hydroxyapatite (HAp) has been of interest for a number of potential applications, including chemical sensors and bone substitutes [5-9]. Nagai et al. [10] examined the surface ionic conduction of HAp for humidity sensor applications, since the room temperature conductivity was influenced by relative humidity. Valdes et al [11] examined the dielectric properties of hydroxyaptite to understand the decomposition of HAp to tri-calcium phosphate (TCP; $Ca_3(PO_4)_2$) as a result of the dehydration of hydroxyl ions at elevated temperatures [12]. This was of interest since TCP is thought to have higher bioactivity than HAp, but is also more biodegradable. Hoepfner et al. [13] reported the influence of porosity on the room temperature permittivity of HAp to understand its interaction with electrical fields. The dielectric properties of polarized HAp have been examined by Takeda et al. [14]. An investigation of the dielectric properties is of interest for biomaterial applications. This has several causes. First, the application of electrical fields can accelerate the healing of fractures in bones [15-17]. Furthermore, an electrical stimulation enhances the rate of bone growth for bone grafts in spinal fusion [18, 19] and is also used to treat osteoarthritis and osteonecrosis [20]. Finally, the electric poling of hydroxyapatite enhances its bioactivity [21]. For all these reasons and because bone is a composite of fluids, collagen and the hydroxyapatite matrix, especially the electric and dielectric properties of hydroxyapatite are very important. In the present work, theoretical calculation of some solid-state dielectric parameters such as total number of valence electron, plasma energy, Penn gap, Fermi energy, electronic polarisability and dielectric susceptibility have been done for HAp. The density was calculated by theoretical method.

2. Theoretical calculation of the density of HAp

The density of HAp is calculated by using the equation

$$\rho = \frac{M\,Z}{N_A V}, \tag{1}$$

where M is molecular weight of HAp, molecular unit cell $Z = 2$, N_A is Avogadro's number, V is volume of the HAp. The theoretical density is found to be 3.161 g cm^{-3}, which is in good agreement with experimental value [22].

3. Dielectric properties of HAp

Generally, the dielectric constant values due to the contributions of electronic, ionic and dipole orientation contributions to the polarizability. The ionic polarization arises from the displacement of ions of opposite sign from their regular lattice sites resulting from the applied electric field as well as deformation of the electronic shells from the relative displacement of the H^+ ions. When the frequency of the applied field is further increased, the dielectric constant decreases. The reason for this may be given that the dipoles are no longer able to rotate sufficiently rapidly so that their oscillations begin to lag behind those of the applied field. As the frequency becomes higher and higher, ionic and orientation source of polarizability decrease and finally disappear due to inertia of ions and a constant value is observed. In discussing the dielectric properties and behavior of insulating materials will be necessary to use some kind of model to represent the dielectric. The Maxwell equations in a polarizable, magnetizable medium, in which also charges are present, can be written in the following form,

$$\nabla \cdot \mathbf{B} = 0, \tag{2}$$

$$\nabla \cdot \mathbf{E} = \frac{1}{\varepsilon_0}\left(\rho - \nabla \cdot \mathbf{P}\right), \tag{3}$$

$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \tag{4}$$

$$\nabla \times \mathbf{B} - \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t} = \mu_0\left(\mathbf{j} + \nabla \times \mathbf{M} + \frac{\partial \mathbf{P}}{\partial t}\right). \tag{5}$$

We neglect magnetization effects, thus setting $\mathbf{M} = 0$. The following relation is always true:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}. \tag{6}$$

Therefore the equations can also be written as,

$$\nabla \cdot \mathbf{B} = 0, \tag{7}$$

$$\nabla \cdot \mathbf{D} = \rho, \tag{8}$$

$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \tag{9}$$

$$\nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = \mathbf{j}, \tag{10}$$

where $\mathbf{B} = \mu_o \mathbf{H}$ in case the magnetization is zero. The charge conservation equation follows from taking the divergence of the last equation, using that $\nabla \cdot (\nabla \times \mathbf{H}) = 0$, and inserting the second equation,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{j}. \tag{11}$$

In the remainder of this section we use Fourier transform language, meaning that all partial derivatives with respect to time are replaced by $-i\omega$

$$\mathbf{j}(\mathbf{r}, \omega) = k(\omega)\mathbf{E}(\mathbf{r}, \omega), \tag{12}$$

where $k(\omega)$ is the frequency constant;

and

$$\mathbf{D}(\mathbf{r}, \omega) = \varepsilon_0 \varepsilon(\omega)\mathbf{E}(\mathbf{r}, \omega). \tag{13}$$

Eliminating density ρ, current $\mathbf{j}$, and $\mathbf{D}$ in virtue of $\mathbf{E}$, we can write these equations as,

$$\nabla \times \mathbf{E}(\mathbf{r}, \omega) - i\omega\mu_0 \mathbf{H}(\mathbf{r}, \omega) = 0, \tag{14}$$

$$\nabla \times \mathbf{H}(\mathbf{r}, \omega) + i\omega \left(\varepsilon_0 \varepsilon(\omega) - \frac{k(\omega)}{i\omega} \right) \mathbf{E}(\mathbf{r}, \omega) = 0, \tag{15}$$

whereas for the charge density,

$$\rho(\mathbf{r}, \omega) = \frac{k(\omega)}{i\omega}\nabla \cdot \mathbf{E}(\mathbf{r}, \omega). \tag{16}$$

Taking once more the curl of Eq. (15), using that

$$\nabla \times (\nabla \times \mathbf{H}) = \nabla(\nabla \cdot \mathbf{H}) - \Delta\mathbf{H} = -\Delta\mathbf{H}. \tag{17}$$

In view of Eq. (10) and the absence of magnetization,

$$-\Delta\mathbf{H}(\mathbf{r}, \omega) + i\omega \left(\varepsilon_0 \varepsilon(\omega) - \frac{k(\omega)}{i\omega} \right) \nabla \times \mathbf{E}(\mathbf{r}, \omega) = 0. \tag{18}$$

Subsequent substitution of Eq. (14) the yields:

$$\Delta \mathbf{H}(\mathbf{r}, \omega) + \frac{\omega^2}{c^2} \left(\varepsilon(\omega) - \frac{k(\omega)}{i\omega} \right) \mathbf{H}(\mathbf{r}, \omega) = 0 . \tag{19}$$

This is a wave equation for the vector field **H**, with dispersion relation,

$$k^2 = \frac{\omega^2}{c^2} \left(\varepsilon(\omega) - \frac{k(\omega)}{i\omega\varepsilon_0} \right), \tag{20}$$

$$\Delta \mathbf{E}(\mathbf{r}, \omega) + \frac{\omega^2}{c^2} \left(\varepsilon(\omega) - \frac{k(\omega)}{i\omega\varepsilon_0} \right) \mathbf{E}(\mathbf{r}, \omega) = \frac{i\omega}{k(\omega)} \nabla \rho(\mathbf{r}, \omega), \tag{21}$$

where we also used Eqs. (15) and (16). This is again a wave equation, now for the electric field with the same dispersion relation as above, but with a source term. The assumption is now that the charges move slowly compared to changes in the electro– magnetic field. In that case we can neglect the source term. Alternatively we can state that the transverse waves are unaffected by the charge distribution, the longitudinal wave probably decay faster as a function of the distance to the sample. A bigger problem is the frequency dependence of k. Assuming that it can be replaces by its zero–frequency value means that the charges can follow the electric field. In the present system, as the frequency increases, a point is reached where the space charge cannot sustain and comply with the external field. Therefore, polarization decreases which exhibits reduction in the values of dielectric constant with increase in frequency [23]. In other words, at high frequency, capacitor offers low reactance to the sinusoidal signal, which minimizes the conduction losses in the resistor and hence, decrease in dielectric constant. The dielectric constant (ε') is determined experimentally by the relation,

$$\varepsilon' = \frac{[C_p t]}{[\varepsilon_0 A]}, \tag{22}$$

where Cp is the capacitance of the sample, t is the thickness of the sample, ε_0 is the permittivity of the vacuum, and A is the area of cross-section of the sample pellet. The dielectric constant of HAp is reported in the literature as 15.4 at 100 Hz [24]. The variation of dielectric properties with respect to frequency reveals the normal dielectric behavior of the material. It is evident from electrical conductivity of the material that the rotation of ions is responsible for conduction process. The conduction mechanism in HA_P is either due to a proton hopping along the c-axis between electroactive O^{2-} anion or to an OH^- ion interacting with the double bonded oxygen of PO_4 groups [25]. On the other hand, OH^- in the lattice of hydroxyapatite is thought to contribute to the ionic concduction at elevated temperature, although the conductivity is relatively low in comparision with other typical ionic conductor [26]. But at room temperature, the surface conduction in HAp is presumed to be mainly caused by migration of proton in adsorbed and/or condensed water [27].

4. Dielectric solid-state parameters
The molecular weight of the HAp is M = 502.31 g/mol, and total number of valence electron Z = 104**.** The density of the HAp ρ = 3.161 g cm^{-3} and dielectric constant at 100 Hz is ε_∞ = 15.4. The valence electron plasma energy, $\hbar\omega_P$ is given by

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}}, \tag{23}$$

where Z is the total number of valence electrons, ρ is the density (g·cm^{-3}) and M is the molecular weight (g) of HAp. The Plasma energy is terms of Penn gap and Fermi energy [28] in eV is given as

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{\frac{1}{2}}} \tag{24}$$

and

$$E_F = 0.2948(\hbar\omega_P)^{\frac{4}{3}}. \tag{25}$$

Polarizability, α is obtained using the relation

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_P^2}\right] \cdot \frac{M}{\rho} \cdot 0.396 \cdot 10^{-24} cm^3, \tag{26}$$

where S_0 is a constant for a particular material, and is given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2. \tag{27}$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation, which is given by,

$$\alpha = \frac{3M}{4\pi\,\rho N_A}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right). \tag{28}$$

Dielectric susceptibility, χ is obtained using the relation:

$$\varepsilon = \frac{\varepsilon_0 E + P}{\varepsilon_0 E} = 1 + \chi \tag{29}$$

or

$$\chi = \frac{P}{\varepsilon_0 E} = \varepsilon - 1, \tag{30}$$

where the symbols have their usual significance. N_A is Avogadro number and the calculated fundamental data of HAp are listed in Table 1. From the results, the polarizability (16.45×10^{-23}) calculated from the solid-state parameters confirms the dielectric behavior of

the material. The HAp shows higher value of electronic polarizability, which is in good agreement with electronic polarizability of Clausius-Mossotti relation.

Table 1. Some solid-state dielectric parameters for HAp.

Parameters	Values
Plasma energy (eV)	23.30
Penn gap (eV)	6.14
Fermi gap (eV)	19.61
Polarizability (cm^3) Penn analysis	$16.45 \cdot 10^{-23}$
Polarizability (cm^3) using Clausius-Mossotti Equation	$16.49 \cdot 10^{-23}$
Dielectric susceptibility (χ)	14.4

5. Conclusion

The solid-state dielectric parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability and dielectric susceptibility of the HAp have been calculated from the measured value of the dielectric constant. The density of HAp is found to be 3.161 g·cm^{-3}, which is in good agreement with experimental value. The dielectric constant increased with at lower frequencies. The proton was expected to play crucial role in the conduction. The higher values of dielectric constant can be explained on basis of this charge compensation. These results might be useful for development of HAp materials for orthopedic applications, perhaps, assisted by electric field of variable frequency.

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