Ferroelectric polarization of hydroxyapatite from density functional theory

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The theoretical ferroelectric polarization of the low-temperature ( monoclinic, P21) phase and the high-temperature (hexagonal, P63) phase of hydroxyapatite Ca10(PO4)6(OH)2 is calculated based on the density functional theory (DFT). In the monoclinic structure, the value of ferroelectric polarization is found to be 9.87 μC cm⁻² along the [001] direction. In the hexagonal structure, the ferroelectric polarization is 7.05 μC cm⁻² along the [001] direction. The main contribution to the electric polarization comes from ordered hydroxyl OH⁻ anions for both phases, although the inorganic Ca5(PO4)3 apatite framework also gives a non-negligible contribution. A detailed analysis of ferroelectric polarization and structural change of the hydroxyapatite is presented for a better understanding of this important biomaterial.

Introduction

Hydroxyapatite (HAp) Ca10(PO4)6(OH)2, the main constituent of human bone and teeth enamel, has been the subject of a considerable number of both experimental and theoretical studies. HAp’s applications span from dental to orthopedic implants, including bone tissue engineering scaffolds, coatings, fillers and many others. Pasteris et al. used laser Raman microprobe microscopy to study the degree of hydroxylation and the state of atomic order of several natural and synthetic calcium phosphates including apatite of biological, geological and synthetic origins. However, a weak OH-band occurs in calcium phosphates including apatite of biological, geological and synthetic origins. Although being one of the prevalently studied biomaterials for orthopedic, dental, protein purification and stem cell applications, there is less research done on the electrical properties of hydroxyapatite. Since the prediction of the possibility of piezo- and pyro-electricity in hydroxyapatite, several experimental and theoretical reports have led to the new level of understanding the electrical behaviors of calcified tissues in vertebrates. Both bone and dentine show interesting electrical properties foremost of which is piezoelectricity, i.e. the possibility of generating electrical charge at the surface when it is subjected to a stress. This surface charge induced by pressure has been considered to be connected with the generation of the bone functional shape in accordance with the Wolff’s law. Bone also possesses a spontaneous dipolar electrical polarization due to its pyroelectric property, which could have functional distribution and physiological effects. Also, the ability to create discrete electrostatic domains on nanocrystalline films of hydroxyapatite will open the possibility of understanding how surface charge influences biological interactions. Kumar et al. presented some results of in vivo experiments in the literature. Positive and negative polarization of HAp plates implanted in calvarial bones of rats resulted in an enhanced osteoblast activity. Also, protein adsorption onto the HAp surface implanted in canine femora and rat tibiae, respectively, resulting in improved osteoconduction on both positively and negatively polarized HAp surfaces in vivo was reported. Though there is evidence that the polarized surface can affect the biological response, further researches are needed to understand the in vivo behaviors of charged HAp surfaces.

The two principal crystalline components of bone are the mineral HAp and the protein collagen, both of which may present piezoelectricity. In the case of HAp, piezoelectricity is due to the polarization of OH⁻ groups confined to the channel formed by the overlapping hexagonal calcium atoms. According to Rietveld analysis carried out on the synthetic sample, HAp has been found to be predominantly hexagonal at room temperature, but the diffraction pattern of this material might be
be interpreted as a mixed phase: 23% monoclinic $P2_1/b$ and
77% monoclinic $P2_1$.

Zahn et al.\textsuperscript{a} carried out molecular dynamics simulation and
verified that the disordering of hydroxide ions orientations
occurs in such a way that collective reorientation of $\text{OH}^-$ ion
rows is not observed. It appears to be a property solely due to the
inherently disordered, nonstoichiometric $P6_3/m$ HAp and not of its
pure, monoclinic, $P2_1/b$ counterpart.\textsuperscript{b} Furthermore, the
crystal structure of stoichiometric HAP is monoclinic ($P2_1/b$),\textsuperscript{4}
but due to foreign ion inclusion, vacancy formation, and Ca\textsuperscript{2+}
depletion, it becomes hexagonal ($P6_3/m$)\textsuperscript{4} for more disordered
biological HAp. Horiuchi et al.\textsuperscript{41} reported experimentally that an
antiferroelectric (AFE) to paraelectric (PE) phase transition
accompanied by a critical slowing down and a sharp increase in
dielectric relaxation strength was not observed at the phase transition.
This implies a weak interaction between the dipoles of the neighboring $\text{OH}^-$ columns. Tofail et al.\textsuperscript{4} employed
calculations with empirical interatomic potentials to show that
nonpolar–polar transition could be induced by temperature. In
2013, Lang et al.\textsuperscript{12} demonstrated that hydroxyapatite exhibits ferroelectricity by using piezoresponse force microscopy.
Recently it was shown that polarized HAp (with an electrically
charged surface) is more active, which is more attractive for
interactions with living cells, attaching more living cells (oste-
oblasts) on its surface.\textsuperscript{10,12,17} Such effect is significant for
medical applications, particularly for implant coatings. Therefore,
more a detailed theoretical study about the ferroelectric (FE) polarization is mandatory. To the best of our knowledge, the
theoretical analysis of ferroelectricity from first principles is
missing in the literature.

In the present paper, we report on the density functional
theory (DFT) study of monoclinic hydroxyapatite and its
hexagonal phase. Our calculation allows the direct computation of the ferroelectric polarization of HAp, an important
information otherwise difficult to access from experimental data.

The paper is organized as follows. First, we give a brief
account of the computational details. Then, we discuss our
results by considering two structures, namely the low-
temperature (monoclinic, $P2_1$) and the high-temperature
(hexagonal, $P6_3$) phases, and their calculated ferroelectric
polarization. The total ferroelectric polarization is further
decomposed into the hydroxyl and calcium apatite contributions.

Computational methods

All investigations were performed using density functional
theory\textsuperscript{31} as implemented in the Vienna ab-initio Simulation
Package (VASP).\textsuperscript{32,33} Kohn-Sham equations were solved using
the projector-augmented-wave (PAW) method with the PBEsol exchange–correlation functional.\textsuperscript{34} The energy cutoff for the
plane waves expansion was set to 600 eV, 4 × 2 × 6 and 4 × 4 × 6
 Monkhorst-Pack grids of $k$ points were used for the mono-
clinic ($P2_1/b$ or $P2_1$) and hexagonal ($P6_3/m$ or $P6_3$) structures respectively. The convergence in total energy and Hellmann–
Feynman forces were set to 1 μeV and 0.01 eV Å\textsuperscript{−1}, respectively.
For all structures, we have chosen the experimentally
determined lattice constant parameters and performed relaxa-
tion of internal atomic positions. The ferroelectric polarization
has been calculated using the Berry phase approach by building
an appropriate PE reference state and considering the suitable
path in the configurational space connecting PE to the FE state.
For the calculation of the ferroelectric polarization, it is
convenient to introduce a reference paraelectric structure, i.e.
centrosymmetric. We can choose for simplicity an antiferro-
electric structure. By comparing the reference structure and the
ferroelectric one and connecting them through an appropriate
linear interpolation of the atomic positions, one can avoid the
spurious presence of polarization quanta, which would lead to
erroneous estimates of polarization. Furthermore, we can also
analyze the atomic displacements responsible for ferroelec-
tricity. In our work, both reference structures are obtained by
displacement of the atomic positions. In particular, we divide
the structures into two parts: one made of distinct hydroxyl units ($\text{OH}^-$), labeled as H, and the other consisting of the
inorganic framework $[\text{Ca}_10(\text{PO}_4)_6(\text{OH})_2]$ , labeled as Ap. In PE structures, for
the H part, the hydrogen and the oxygen atoms are equally
distributed along [001] direction, forming a paraelectric
arrangement of O and H atoms. At the same time, we also
transform the inorganic framework Ap into a centrosymmetric
structure. Therefore, the FE state ($\lambda = 1$) is obtained from the
centric ($\lambda = 0$) state by shifting of the different functional
groups.

The ferroelectric polarization is defined as $\Delta \mathbf{p} = \mathbf{P}_{\text{FE}} - \mathbf{P}_{\text{PE}} = \Delta \mathbf{P}_{\text{ion}} + \Delta \mathbf{P}_{\text{el}}$, where $\Delta \mathbf{P}_{\text{ion}}$ is the sum of the products of the devi-
tions in the position of each ion in the unit cell (with respect to
the centric reference phase) with the nominal charge of its rigid
core; the electronic contribution $\Delta \mathbf{P}_{\text{el}}$ has been calculated by using the Berry phase approach\textsuperscript{35,36} which correctly accounts for
quantum-electronic effects. Graphical rendering of the crystal
structures was performed using VESTA.\textsuperscript{37}

Results

The HAp unit cell lattice parameters are fixed at experimental
values\textsuperscript{a} $a = b = 9.423$ Å and $c = 6.883$ Å for the high-
temperature (hexagonal, $P6_3/m$) phase, and $a = 9.426$ Å, $b =
18.856$ Å and $c = 6.887$ Å for the low-temperature (mono-
clinic, $P2_1/b$) phase as shown in Table 1 and Fig. 1. The
hexagonal HAp phase consists of 44 atoms in the unit cell,
while the monoclinic HAp structure has 88 atoms because the
unit cell is doubled along the $b$ axis. For the low-
temperature (monoclinic, $P2_1$) and the high-temperature

Table 1 Experimental lattice parameters\textsuperscript{28} of the hydroxyapatite crystal used in our present DFT calculation

| $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ | Lattice parameters |
|-----------------------------------|--------------------|
| Crystal symmetry                  | $a$/Å   | $b$/Å   | $c$/Å   | $\alpha$/° | $\beta$/° | $\gamma$/° |
| $P6_3/m$; polar $P6_3$           | 9.423   | 6.883   | 90      | 90         | 120       |
| $P2_1/b$; polar $P2_1$          | 9.426   | 18.856  | 6.887   | 90         | 90        | 119.97     |
(hexagonal, $P_{6_3}$) structures, the atomic positions have been relaxed under fixed experimental lattice parameters. We introduce in the modeling two new structures, $P_{2_1}/b$, and $P_{6_3}/m$ space group as reference centrosymmetric lattices, shown in Fig. 2. Here, a schematic representation of the OH electric dipole displacement from paraelectric to the ferroelectric configuration is illustrated. We caution the reader that only the polarization for $\lambda = 1$ has a real physical meaning, while the intermediate values are only computational states which allow monitoring the continuous evolution of the polarization as a function of $\lambda$, thus excluding the inclusion of quanta of polarization. We have also done additional calculations for the centrosymmetric configuration while keeping the O–H bond as what it is. We relaxed the structure and compared its energy with non-centrosymmetric phase, confirming that the energy difference between them is about 0.02 eV per unit cell and the ferroelectric phase is slightly higher in energy. The Fig. 3 shows a variation of the electric polarization of $P_{6_3}$ (left) and $P_{2_1}$ (right) structures as a function of the normalized amplitude of the polar distortion between centric ($\lambda = 0$) and polar ($\lambda = 1$) configurations.

It is useful to separate the polarization contributions coming from the two parts: the floppy component (OH$^-$), (the H sublattice), and the inorganic framework [Ca$_5$(PO$_4$)$_3$]+, namely Ap. Then, we evaluate the FE polarization. Here HAp means the total value of ferroelectric polarization by considering the correlated distortions of the H and Ap together; H means the FE value of OH$^-$ by considering the centrosymmetric inorganic framework; Ap means the FE value of [Ca$_5$(PO$_4$)$_3$]+ under centrosymmetric OH$^-$ lattice; H + Ap means the simple algebraic summation of H and Ap. These results are displayed in the Fig. 4.
Discussion

The hydroxyapatite structure consists of a pseudo-hexagonal network ofapatite’s tetrahedra with Ca$^{2+}$ ions in the interstitial sites and columns of anions oriented along the c axis. Based on previous refinements of diffraction data, two phases have been suggested: a disordered hexagonal structure with P6$_3$/m symmetry and a monoclinic structure with P2$_1$/$b$ symmetry. The monoclinic unit cell is derived from two hexagonal unit cells with the $b$ axis parameter being twice that of the hexagonal value and involves an ordered arrangement of the anion columns. It has been proposed that the monoclinic phase is associated with stoichiometric apatites.

In order to study the ferroelectric order, we consider a paraelectric (centric) structure in terms of which one can present the polar crystal structure as due to symmetry-lowering structural distortion from the high symmetry centric group. It is useful to introduce a parameter $\lambda$ which is the normalized amplitude of the distortion connecting the centric to the polar structure: $\lambda = 1$ represents the compound in the P6$_3$ or P2$_1$ space group, $\lambda = 0$ represents the compound in the P6$_3$/m or P2$_1$/$b$ space group, respectively. We found that the systems have FE polarization of $P = -7.05 \mu$C cm$^{-2}$ and $-9.87 \mu$C cm$^{-2}$ along $c$ axis for the hexagonal and monoclinic cases, respectively. Experimentally, the remnant polarization in hydroxyapatite film is ca. 25% of a PZT film, which possesses a polarization value of about 20–70 $\mu$C cm$^{-2}$. Our calculated results (7–10 $\mu$C cm$^{-2}$) are very close with such experimental report.

We now discuss in more detail the separate role of the H and Ap on the polarization of the different HAp structures by fixing the centrosymmetric inorganic framework or by fixing the centrosymmetric OH$^-$ lattice, respectively. For P$6_3$ structure, we obtain the total polarization $P$(HAp) = $-7.05 \mu$C cm$^{-2}$ from the fully relaxed structure. Assuming that the inorganic framework is centrosymmetric, we find the OH$^-$ dipoles to be $P$(H) = $-10.41 \mu$C cm$^{-2}$. On the other hand, when fixing the OH$^-$ coordinates to be centrosymmetric, the $P$(Ap) = 2.48 $\mu$C cm$^{-2}$ value is obtained, provided by the [Ca$_5$(PO$_4$)$_3$]$^{2-}$ sublattice. Finally, we have a simple algebraic summation of $P$(Ap) + $P$(H) = $-7.93 \mu$C cm$^{-2}$ which is close to the total polarization. For P$2_1$ structure, similarly we have total polarization $P$(HAp) = $-9.87 \mu$C cm$^{-2}$, while the separate $P$(H) = $-8.74 \mu$C cm$^{-2}$ and $P$(Ap) = $-0.80 \mu$C cm$^{-2}$, and $P$(Ap) + $P$(H) = $-9.54 \mu$C cm$^{-2}$ as well.

The origin of the different polarization values of these two structures can be understood. We note that the difference of the polarization value of the two polar structures is not too large, for the P6$_3$ and P2$_1$ structures. From calculated polarization of H and Ap components for the two structures, we found that the Ap contributes to the polarization difference more than the H part, even though Ap has only a small contribution to the total polarization.

The main mechanism for the transformation of P6$_3$ into P2$_1$, is that the [PO$_4$]$^{3-}$ tetrahedron structure of Ap has a rotation of about 5° in monoclinic phase. The difference of H is mainly due to the variation of bond length between oxygen and hydrogen, the bond length of OH$^-$ is 1.05359 Å in P6$_3$ and 1.01883 Å in P2$_1$, which results in different polarization values. For P6$_3$, the polarization of H should be larger than that of P2$_1$, but the polarization of Ap is opposite in sign, therefore the total polarization of P6$_3$ is smaller than that of P2$_1$.

Conclusions

We have analyzed the ferroelectric polarization of the low-temperature (monoclinic, P2$_1$) phase and the high-temperature (hexagonal, P6$_3$) phase of hydroxyapatites, on the basis of density functional theory calculations and the modern theory of ferroelectric polarization. We decomposed the total dipole moment contributions into hydroxyl groups and calcium phosphate apatite framework. The major polarization is from ordered hydroxyl anions for both phases. However, the inorganic [Ca$_5$(PO$_4$)$_3$]$^{2-}$ may have a sign change for polarization between these two polar structures. Detailed analysis of ferroelectric polarization and structural change of the HAp is provided. Our DFT results are useful for the better understanding of this important biomaterial in many actual and prospective applications.

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