Atomistic Simulation Study of the Order/Disorder (Monoclinic to Hexagonal) Phase Transition of Hydroxyapatite

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The transformation of the low-temperature (monoclinic, $P2_1/b$) to the high-temperature (hexagonal, $P6_3/m$) modification of hydroxyapatite—$Ca_5[(OH)(PO_4)_3]$—is investigated by means of molecular dynamics simulations. In the monoclinic phase the orientation of the hydroxide ions is strictly ordered. Above the critical temperature of about 200 °C orientational changes of the hydroxide ions are observed. In the course of each reorientation event a hydroxide ion passes through the surrounding calcium triangle. From an Arrhenius fit the related activation energy is calculated. In the high-temperature phase the hydroxide ions are statistically disordered. Out of the two possible concepts for the formation and structure of hexagonal hydroxyapatite, our simulations clearly identify the disordering of hydroxide ions orientation to occur in a nonconcerted manner, i.e., collective reorientation of OH^- ion rows is not observed.

Introduction

Hydroxyapatite—$Ca_5[(OH)(PO_4)_3]$—has been subjected to a considerable number of both experimental[1−5] and theoretical studies.[6,7] It is the predominant component of human bones[8] and teeth.[9] Among other factors, it is reasonable to assume that the arrangement of the OH^- dipoles influences the apatite crystal morphology.

Depending on its preparation conditions (at room temperature) pure hydroxyapatite is found to have either monoclinic (space group $P2_1/b$; $a = 9.4214(8)$ Å, $b = 2a$, $c = 6.8814(7)$ Å, $\beta = 120.00(8)°$, $Z = 4$)[1] (Figure 1, top) or hexagonal (space group $P6_3/m$; $a = b = 9.432$ Å, $c = 6.881$ Å, $Z = 2$)[4] symmetry (Figure 1, bottom). The latter corresponds to the high-temperature modification, which can be obtained via an order/disorder transition from the low-temperature phase. By means of optical birefringence experiments,[2] X-ray, and difference scanning calorimetry measurements this transformation was observed at temperatures above ∼200 °C.[3] From crystal structure determinations of hexagonal hydroxyapatite an occupation of 0.5 for each crystallographic OH^- position is obtained as an average over the whole crystal.[4] Two different models are discussed for the high-temperature phase in attempt to explain the (average) hydroxide ion orientation within the channels formed by calcium triangles (Ca2 in Figure 1). The mirror plane perpendicular to the *c* axis of the space group $P6_3/m$ may be associated to (*i*) a "disordered column" model in which the orientation of the hydroxide ions is inverted at random sites within the channels, or (*ii*) an "ordered column" model in which all OH^- ions in a single row point in the same direction, while the overall orientation of each column is randomly distributed.[4]

Both models are indistinguishable by X-ray or neutron scattering experiments and which picture accounts for the hexagonal modification of hydroxyapatite could not be revealed so far.[5] In the present paper, we report on a molecular dynamics simulation study of the order/disorder phase transition of monoclinic hydroxyapatite to its hexagonal modification. Although difficult to access from experimental data, our atomistic model allows the direct observation of the hydroxide ion arrangement and hence the formation and structure of the hexagonal phase of hydroxyapatite.

Simulation Details

A block of 4 × 2 × 5 unit cells (∼37.7 Å × 37.7 Å × 34.4 Å) of monoclinic hydroxyapatite was chosen as simulation model. Periodic boundary conditions were applied in all directions. The semi-flexible apatite model of Hauptmann et al.[6] was applied, in which the intermolecular interactions are described by a combination of Coulomb− and Born−Mayer−Huggins potential terms. The apatite model was parametrized with respect to high-temperature properties and is hence particularly suited for the simulations reported in the present work.[6] The molecular dynamics simulations were

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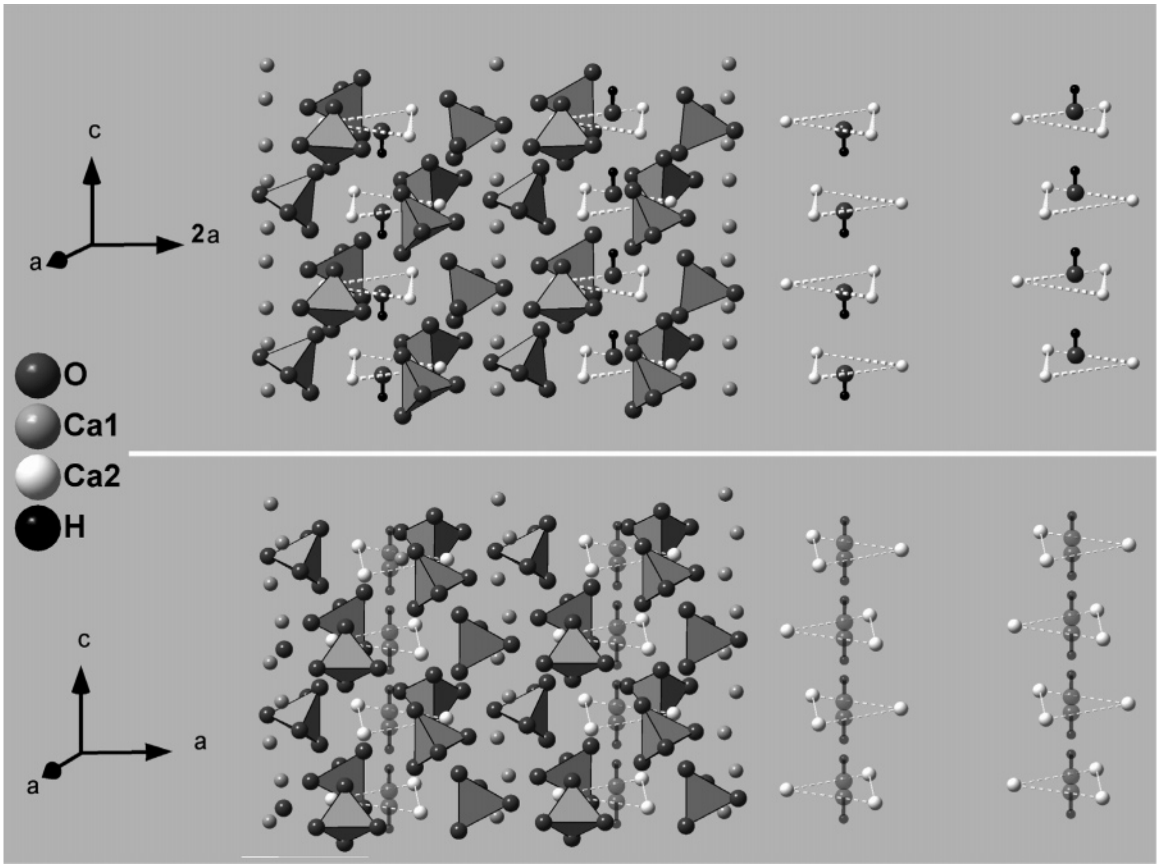

Figure 1. Clippings taken from the crystal structures as known from neutron and X-ray scattering of monoclinic (top) and hexagonal (bottom) hydroxyapatite. The phosphate ions are represented by tetrahedra, and the calcium triangles (Ca2) embedding the hydroxide ions are indicated by dashed lines. On the right side, the calcium channels are highlighted. In hexagonal hydroxyapatite, the occupancy of the hydroxide ions above and below the pseudo-mirror plane is 0.5 (represented as half transparent OH^- ions).

performed using the DLPOLY package.[10] Ewald summation was applied for treatment of the Coulomb interactions. Our simulations were done in the NpT ensemble at atmospheric pressure and in a range of various temperatures. The Melochionna thermostat–barostat combination was applied allowing cell shape variations so as to not impose symmetry restrictions.[11] A time step of 1 fs was found to be appropriate. For each temperature investigated the ideal monoclinic modification related to zero Kelvin in combination with initial velocities according to Maxwell distribution corresponding to the desired temperature was used as the starting configuration. A relaxation period of 30 ps was found to be appropriate to ensure convergence of the simulation volume. While this reflects some relaxation, the system cannot reach equilibrium within this short period. The (slower) process of hydroxide ion orientation disordering was studied from a series of 7 or more subsequent 100-ps trajectories taken after convergence of the simulation cell dimensions.

Results

As a starting point we set up a series of molecular dynamics runs of monoclinic hydroxyapatite at 100, 200, ..., 1200 °C. At 100 °C the simulation system remained in the monoclinic modification of hydroxyapatite with the hydroxide ions being arranged in ordered hydrogen-bonded chains along [001] (Figure 1, top). However, at 200 °C two hydroxide reorientation events were observed during a 700 ps run. Though representing at least the beginning of the disordering process the hydrogen bonded chain remained—much longer simulation periods would be needed to observe a full transformation of the monoclinic to the hexagonal phase. At 300 °C the kinetics of this process is considerably enhanced and a total number of $n_{\text{flip}} = 26$ flips was counted. In Figure 2 an Arrhenius plot of the number of orientation inversion events observed at $T \geq 300$ °C is shown. From this, the activation energy of the OH^- reorientation process is obtained as 50 kJ/mol.

The two possible structural models of hexagonal hydroxyapatite differ in the arrangement of the OH^- ions. It may be expected that our simulation model tends to favor parallel hydroxide orientation within single rows, as the periodic boundary conditions imply an additional coupling. Each row contains 10 explicitly modeled OH^- ions, resulting in an artificial correlation of 10 ions in the hydrogen bond network. Despite this model artifact, in our simulations the flips were found to occur in a nonconcerted manner, hence the reorientation of entire columns of hydroxide ions could not be observed. Instead, we find the overall disordering of hydroxide ion orientation in the hexagonal phase to take place within each single row. To illustrate this phenomenon we calculated the average number of adjacent hydroxide ions along [001] oriented in the same way (Figure 3). Each

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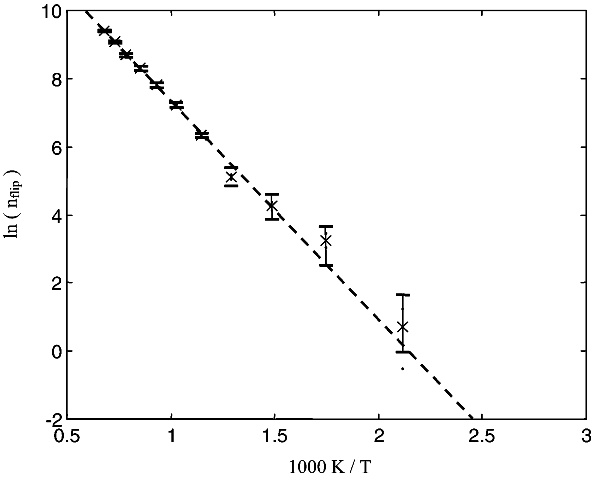

Figure 2. Arrhenius plot of the number of OH^- reorientation events during sampling periods of 7 × 100 ps. The error margins are taken as the root-mean-square deviations resulting from 7 independent sampling intervals of 100 ps. The simulation model counts a total of 160 hydroxide ions.

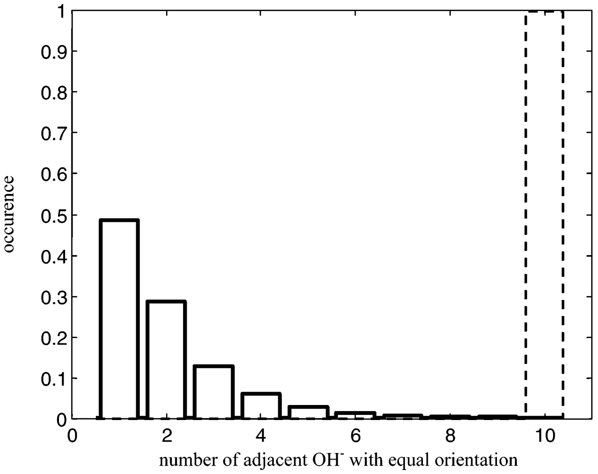

Figure 3. Occurrence profile taken for the number of adjacent hydroxide ions with equal orientation (solid bars). The periodic boundary conditions of the simulation model constitute a maximum number of 10 OH^- ions of parallel arrangement (dashed bar).

700 ps run was started from the monoclinic modification of hydroxyapatite, with all OH^- ions being strictly ordered initially. As a consequence the number of hydroxide ions forming a chain of equally oriented ions is 10, which is the maximum value allowed in our model (dashed bar). In the course of time propagation a large number of hydrogen bonds are broken. The solid bars in Figure 3 show the occurrence profile of the number *n* of adjacent OH^- ions with equal orientation after convergence is reached. The curve roughly matches $(^1/_2)^n$, indicating that half of the hydroxide ions are oriented antiparallel with respect to their nearest neighbors along the [001] direction. Once the occurrence profile takes this form, the rate of flips resulting in parallel and antiparallel neighbor orientations is balanced and the hexagonal phase reached its equilibrium. While the plot is shown for the simulation run at 800 °C, the corresponding curves for 300 °C $\le T \le$ 1200 °C are basically identical. They do however differ in the simulation time needed to obtain convergence in the occurrence profile of hydroxide orientation. For instance, at 300 °C the simulation run had to be extended to 3 ns in order to approach convergence. At 200 °C the kinetics are too slow to observe a full relaxation of hydroxide orientation within a reasonable simulation time. Nevertheless, we assume the structure of the hexagonal phase of hydroxyapatite at $T \le$ 200 °C to be qualitative identical to those observed at higher temperatures. This is supported by the linear shape of the Arrhenius plot shown in Figure 2, indicating no change in the OH^- flipping mechanism within the interval 200 °C $\le T \le$ 1200 °C. From simulations at $T <$ 200 °C starting at the hexagonal phase, we could not observe a transition to the monoclinic structure. This may be related to a large hysteresis effect caused by the short simulation times of some ns accessible to our simulations.

A trajectory exhibiting a hydroxide reorientation event is illustrated in Figure 4. The reorientation mechanism involves passing of the OH^- ion through the triangle formed by calcium ions (blue, Ca2 in Figure 1). As an intermediate state, the hydroxide ion is oriented parallel to the calcium triangle. This arrangement has a very short lifetime and the overall flipping process typically occurs within about 50 fs. In the intermediate configuration the oxygen atom (red) points toward one of the calcium ions, while the positively charged hydrogen atom (green) crosses the opposite edge of the triangle. In the course of the orientation inversion of the central hydroxide ion in Figure 4, a situation occurs in which two hydroxide ions are at close distance. Assuming the OH^- positions to be identical to those in the average crystal structure of hexagonal hydroxyapatite (Figure 1, bottom), both hydrogen atoms would point toward each other and exhibit a distance of only about 0.5 Å. To avoid such an unfavorable configuration, the orientation of these hydroxide ions deviates by 20−40° from the [001] direction. In average the O••O, O••H, and H••H distances were found as 2.4, 1.5, and 1.5 Å, respectively.

The temporary widening of one edge of the calcium triangle, which is penetrated by a hydroxide ion, is somewhat hard to observe from Figure 4. We therefore plot the occurrence profile of the distances between the calcium ions of the triangles embedding the hydroxide ions (Figure 5). While the dotted curve shows the overall Ca••Ca distance distribution, the solid curve corresponds to those Ca••Ca distances related to flipping events only. The latter statistics was accomplished by cutting sketches of 50-fs duration (from 25 fs before to 25 fs after the crossing of the intermediate state) of the trajectories of those calcium triangles in which a flipping event occurs. From integration of the two peaks of the solid curve, we can identify two Ca•••Ca distances at 4.0 Å and one at 4.4 Å. Hence, the distance of the two calcium ions forming the edge through which the hydroxide ion passes typically increases by 0.4 Å, while the other edges are only marginally changed. From this, the stretching of one edge of the calcium triangle may be seen to be a necessary condition for the orientation inversion event of the embedded hydroxide ion.

To estimate the transition temperature of the monoclinic ↔ hexagonal transformation, one might relate the defect energy ΔE_{flip} caused by a single hydroxide orientation inversion to the gain in entropy $k_B T \ln 2$ associated with doubling the number of possible OH^- arrangements. Ignoring the volume term, the transition temperature results from $\Delta E_{\mathrm{flip}} = k_B T_{\mathrm{transition}} \ln 2$. However, we found that the defect

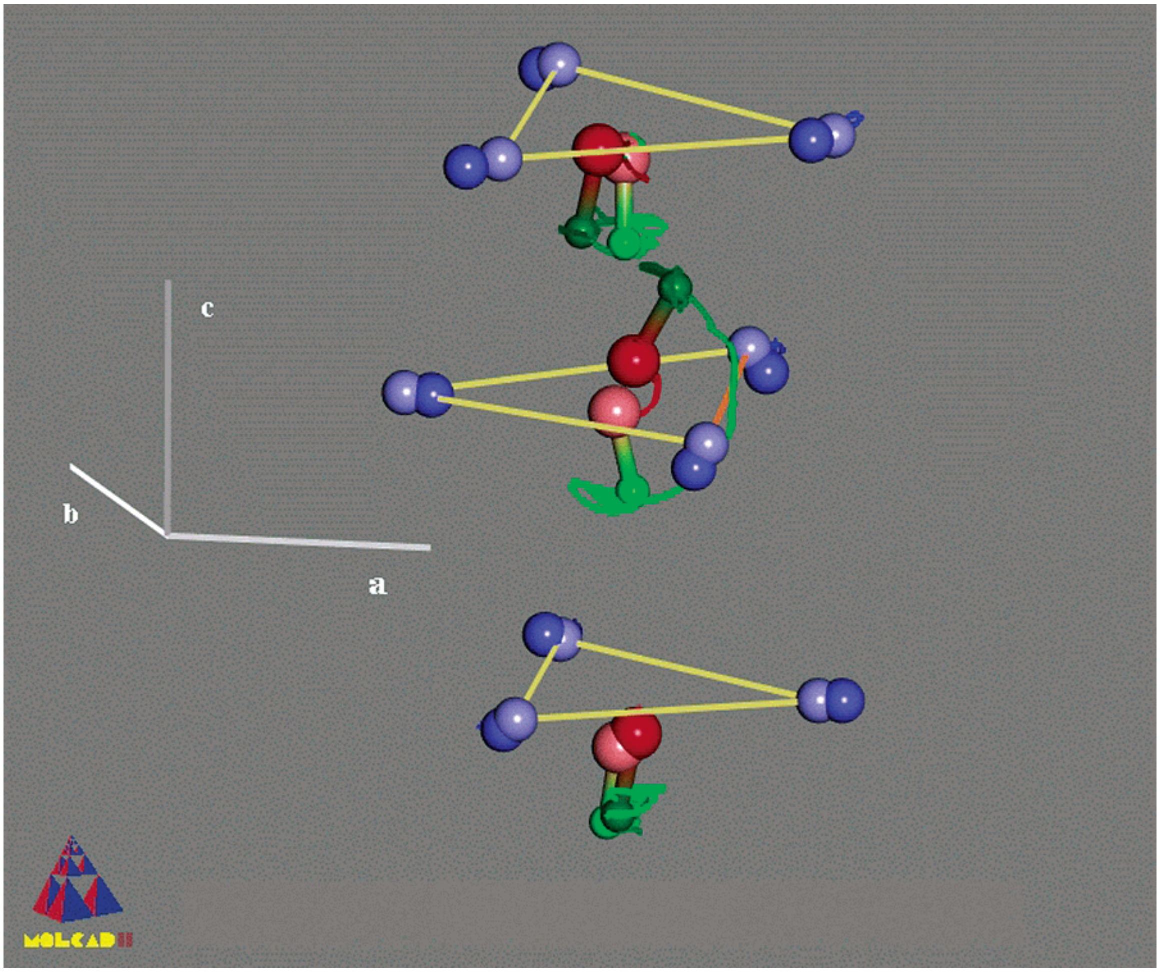

Figure 4. Illustration of a representative trajectory exhibiting a hydroxide orientation inversion event. The configurations 150 fs before and 150 fs after the flipping event are shown in ball-and-stick representation (in bright and dark colors, respectively). The curves connecting the initial and the final ionic positions indicate the corresponding pathways. The calcium triangles of the initial configuration are illustrated in yellow, and the edge which a hydrogen atom crosses during the hydroxide orientation inversion is highlighted in orange.

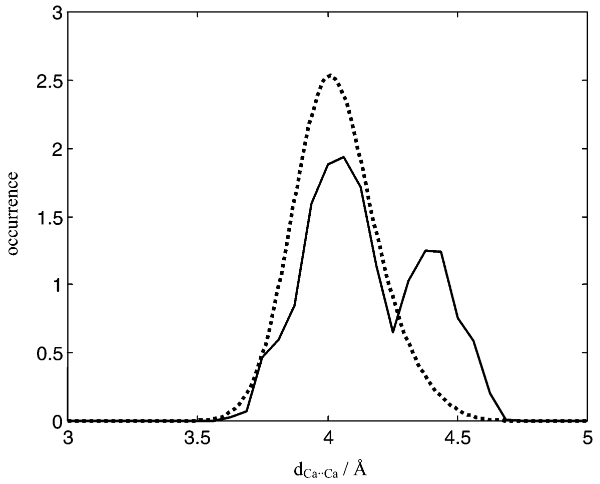

Figure 5. Occurrence profile of the distances of the calcium ions of the triangles embedding the hydroxide ions at 500 °C. The solid curve corresponds to flipping events only, and the dotted curve reflects all data.

energy dramatically depends on the volume of the simulation cell. The defect energy computed from energy minimization, i.e., structures at zero Kelvin is in the order of 100 kJ/mol. On the other hand, we compared the average potential energy of our simulation system at 200 °C before and after a hydroxide inversion event. The related difference in energy was found to be less than 10 kJ/mol. The latter is the accuracy accessible to our sampling of the average potential energy, which fluctuates as a consequence of exchanging kinetic and potential energy in the finite system.

Conclusion

We presented a molecular dynamics study of the order/disorder phase transition (monoclinic to hexagonal) of hydroxyapatite. In the monoclinic phase the orientation of the hydroxide ions is strongly ordered. Above the transition temperature of ∼200 °C the mobility of the hydroxide ions is drastically increased and the crystal transforms to the hexagonal modification. At these conditions the hydroxide ions were observed to frequently pass through the surrounding calcium triangles and hence inverse their orientation. From our simulations the flips were found to occur in a nonconcerted manner, hence the reorientation of entire rows of hydroxide ions could not be observed. Instead, the disordering of the hydroxide ion arrangement involves breaking of the order within each row of OH^- ions along the [001] direction. From an Arrhenius plot the activation energy for the flipping of a hydroxide ion was calculated as 50 kJ/mol.

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