

## Reorientation phenomena of hydroxide ions in monoclinic hydroxyapatite

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### 1. Research Object

Hydroxyapatite (HAp;  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is the most well-known inorganic material in the biomedical field. As its name suggests, HAp contains hydroxide ( $\text{OH}^-$ ) ions. The behavior of  $\text{OH}^-$  ions is regarded as an origin of peculiar properties of HAp[1]. HAp also has interesting electric properties. HAp exhibits proton conductivity[2], ferroelectric-like properties[3], and electret properties[4–6]. These electric properties in HAp are expected to open up new possibilities of HAp application, which is expected to connect bioengineering and electronics. Such intriguing properties in HAp are regarded as ascribed to  $\text{OH}^-$  ions, which form one-dimensional chains in the crystal lattice. In stoichiometric hydroxyapatite, the arrangement of  $\text{OH}^-$  ions becomes ordered, while that is disorderd in non-stoichiometric hydroxyapatite. The hydroxyapatite with ordered  $\text{OH}^-$  ions is named monoclinic hydroxyapatite which has an antiferroelectric-like structure as shown in Fig.1(a). The  $\text{OH}^-$  ions in one column are ordered in a direction that is opposite to those of neighboring columns. Biological apatites are non-stoichiometric and have hexagonal structures shown in Fig.1(b), where the up and down side of the  $\text{OH}^-$  orientations are disordered. The orientations of dipoles of the  $\text{OH}^-$  ions in the chains dominate the electric and surface properties of HAp. In this study, we focused on the  $\text{OH}^-$  motion in monoclinic hydroxyapatite. The monoclinic structure which is stable at room temperature changes to hexagonal at the phase transition temperature of 483 K. In this study, we specifically examine the reorientation motion of  $\text{OH}^-$  ions near the phase transition temperature. Dielectric permittivity was measured at RT–573 K and the  $\text{OH}^-$  ion motions across the phase transition were evaluated.

### 2. Experimental Results

HAp ceramics with monoclinic structure were fabricated from HAp powder synthesized using a wet method from analytical grade calcium hydroxide and phosphoric acid. The pressed green pellets were heated at 1473 K for 0.5 h, cooled to 1273 K, and kept for 20 h. The heating processes were performed under flowing oxygen gas saturated with water vapor. The 7-mm-diameter ceramic disks were obtained. The crystal structure was confirmed using a powder X-ray diffraction method, which suggests that sintered HAp pellets have monoclinic structure. All peaks are assigned to the monoclinic HAp structure (ICDD PDF 01-076-0694). No secondary phases were detected. In measured infrared (IR) spectrum suggests that the sintered pellet does not contain carbonate.

Figures 2(a) and 3(b) respectively present spectra of the real and imaginary parts of relative permittivity as a function of frequency on logarithmic scales. The spectra are shifted vertically for clarity. The two-step dispersions are found. For clarity, the relaxations at low and high frequencies are designated respectively as Relax\_L and Relax\_H. The two-step dispersion spectra were deconvoluted by fitting calculations that are based on the assumption that the dispersion could be expressed by sum of Debye-type relaxation. The solid lines are calculated and dots are experimental data. Good fits are obtained in Fig. 2(a) and 3(b).

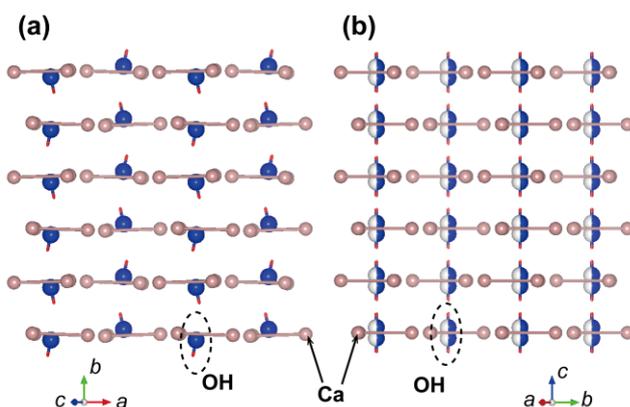


Figure 1(a) Real part and (b) imaginary part of relative permittivity, as a function of frequency.

Relaxation times for Relax\_L and Relax\_H obtained from the fitting calculations are shown as a function of inverse temperature in Fig. 3. The activation energies calculated from the slopes using Arrhenius equation. The values are shown in the figure. Most noteworthy is that  $\tau_H$  has a discontinuity near the phase transition temperature (483 K). The  $\tau_H$  at lower and higher temperature ranges are 0.74 eV and 0.43 eV. Additionally, the  $\tau_H$  of monoclinic HAp are more than ten times larger than that of hexagonal HAp (shown as thick line). Relax\_H is ascribed to the reorientations of OH<sup>-</sup> ions[7]. Therefore, the behaviors of the  $\tau_H$  show the difference of OH<sup>-</sup> ion motions between monoclinic and hexagonal HAp. The OH<sup>-</sup> ion mobility was increased by the phase transition of monoclinic to hexagonal. In other words, the OH<sup>-</sup> ion motion is slowed in monoclinic HAp. This brake originates from the antiferroelectric structure. The interaction between the electric dipoles of OH<sup>-</sup> ions hides the reorientational motions. At temperatures higher than 483 K, the OH<sup>-</sup> ion motion accelerates because the monoclinic HAp transforms into the hexagonal HAp which has disordered OH<sup>-</sup> ions. Biological apatites usually contain fewer OH<sup>-</sup> ions and more defects than the stoichiometric HAp. The OH<sup>-</sup> ion defects induce the phase transition of monoclinic to hexagonal. Recently, some biological apatites with ordered OH<sup>-</sup> ions have been reported.[8] Biological organisms might be able to use the ordered-disordered phase transition to control the properties of HAp. As our results suggest, the disorder of OH<sup>-</sup> ions accelerates the motion of OH<sup>-</sup> ion and enables more flexible movement, which might promote interfaces between biological apatites and extracellular molecules.

### 3. References

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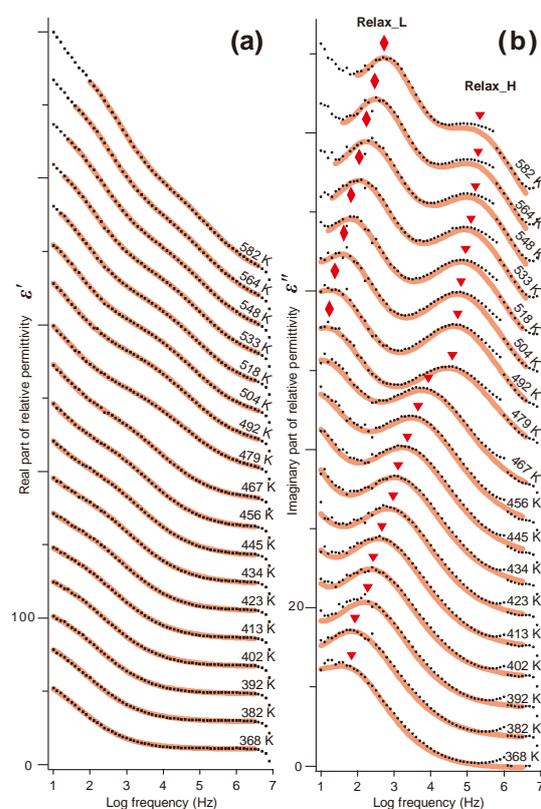


Figure 2(a) Real part and (b) imaginary part of relative permittivity, as a function of frequency.

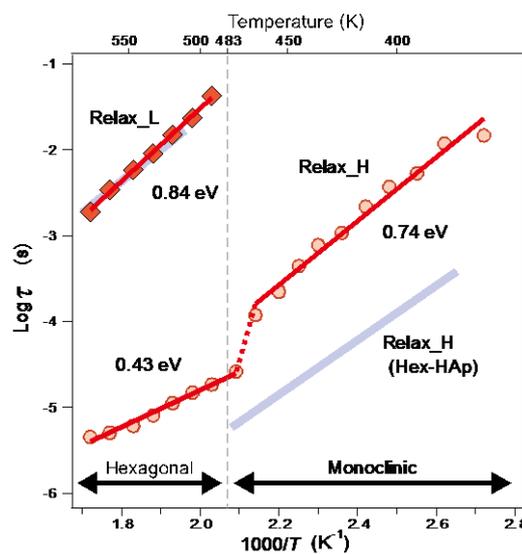


Figure 3 Arrhenius plot of relaxation times. Blue thick lines are from ref [7].