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Ab initio elastic properties and tensile strength of crystalline hydroxyapatite

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Abstract

We report elastic constant calculation and a ‘‘theoretical’’ tensile experiment on stoichiometric hydroxyapatite (HAP) crystal using an ab initio technique. These results compare favorably with a variety of measured data. Theoretical tensile experiments are performed on the orthorhombic cell of HAP for both uniaxial and biaxial loading. The results show considerable anisotropy in the stress–strain behavior. It is shown that the failure behavior of the perfect HAP crystal is brittle for tension along the *z*-axis with a maximum stress of 9.6 GPa at 10% strain. Biaxial failure envelopes from six ‘‘theoretical’’ loading tests show a highly anisotropic pattern. Structural analysis of the crystal under various stages of tensile strain reveals that the deformation behavior manifests itself mainly in the rotation of the PO_4 tetrahedron with concomitant movements of both the columnar and axial Ca ions. These results are discussed in the context of mechanical properties of bioceramic composites relevant to mineralized tissues.

Keywords: Hydroxyapatite; Mechanical properties; Elastic constants; Tensile strength

1. Introduction

Collagen and apatitic mineralites can form complex composite structures that have remarkable mechanical properties and are thus the two primary building blocks of most hard tissues [1,2]. Detailed and accurate structure–property–function relationships of apatitic mineralites, collagen and their composites are critically important for evaluating the mechanical properties of bone and dentin structures, for understanding diseased states of mineralized tissues, and for establishing biomimetic material-design principles. Most mineralized tissues, such as bone and dentin, are organized hierarchically in terms of composition, structure and properties, and they exhibit multiscale structure/property interdependence (molecule/crystallite to fibril to fiber, etc.). Over the decades, intense research has been performed to understand the behavior of these materials at different hierarchical scales [3–10]. The significant role that biological apatite(s) play in the structure and function of calcified tissues was recognized as far back as the early part of the last century [11]. The composition and crystal structure of biological apatite(s) and their implication for function have since been a subject of continuous investigation [11–15]. Recent investigations and data interpretations have also linked apatite composition properties to aging and disease [16,17].

Many computational and experimental studies performed at different spatial scales on a prototype bioceramic, hydroxyapatite (HAP), and the related carbonated HAP, which is more relevant to biological environments, have advanced our understanding of mineralized tissue. However, details of the atomic-scale interactions that are at the heart of the mechanical properties remain as critically missing pieces of information. Clearly, in the absence of such information our understanding of calcified tissue behavior will remain incomplete. Only recently have researchers begun to address the problem at this scale

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[18]. The various efforts to relate mineralized tissue mechanical properties to constituent phase show that simple consideration of composition is insufficient. One of us (A.M.) has recently performed homotopic (same location and lateral resolution) microscale density–composition–elastic modulus measurements on human dentin [19] and showed that, at the same mineral volume fraction and density, the elastic modulus can vary by as much as a factor of five. Similar results have also been found for bones and calcified cartilage based upon nanoindentation [20,21]. While qualitative and subjective explanations abound, there is a distinct absence of quantitative theories and reliable data.

The key obstacle hampering further progress is a lack of understanding of the mechanical behavior in terms of atomic-scale mechanisms. With recent advances in computational capabilities, it is now possible to investigate the mechanical behavior of complex multi-atom systems using large atomic models (of the order of 1000 atoms) and ab initio methods [22–25]. In this paper, we report the results of the mechanical properties of stoichiometric HAP crystal using a highly accurate ab initio technique. The goal is to demonstrate that the atomic structure has a large influence on the anisotropy of the mechanical behavior, leading to significantly different failure behaviors. Such data are crucial for explaining the directional dependence of the alignment of mineralites in collagen fibrils and is the first step towards deeper understanding of collagen/apatite composites that are important to the biological and biomedical community. The implication is that similar ab initio studies along these lines will provide important fundamental insights for furthering our understanding of the mechanical behavior of composite material at the tissue level.

In this work, we report the elastic constants and bulk properties of perfect crystalline HAP and have carried out uniaxial and biaxial "theoretical" tensile experiments to investigate the deformation and failure behavior of HAP under strain. We briefly outline the method of simulation in Section 2; Section 3 describes the results obtained and these results and their implications are further discussed in Section 4. The paper ends with some conclusions in Section 5.

2. Method of simulation

2.1. Crystal structure

The HAP crystal has a fairly complex structure with 44 atoms in the hexagonal primitive cell [26] (two formula units of $Ca_5(PO_4)_3OH$, space group $P6_3/m$ and a 50% partial occupancy of the OH sites). The crystal consists of tightly bonded PO_4 tetrahedral units, two types of Ca ions and the OH groups. The OH is aligned along the crystalline c-axis. There are two Ca sites, Ca1 and Ca2, that are usually labeled as columnar Ca and axial Ca, respectively, and which play the role of ionically bonding the PO_4 units together. For O ions, there are three crystallographically nonequivalent sites. O1 and O2 have 6 sites and O3 has 12 sites. In most bioceramics the Ca/P ratio is usually used to characterize the sample [27]. This value is 1.666 for stoichiometric HAP but the real samples in laboratory experiments usually can have Ca/P ratios either larger or smaller than this value, indicating the difficulty in obtaining pure samples for this quite common bioceramic material. In carbonated HAP, where the CO_3 group replaces the PO_4 group, the Ca/P ratio would be much higher due to the reduction of P. However, in most defective samples where vacancies or Ca deficiencies exist, the Ca/P ratio can be in the range of 1.5–1.67. In tri-calcium phosphate, $Ca_3(PO_4)_2$, another important bioceramic, the Ca/P ratio is 1.5.

The electronic structure and bonding of the HAP crystal has been studied by several groups in recent years [28–31]. We have also studied the surface structure and surface electronic structure of HAP and fluorapatite (FAP) crystals [30]. More recently, ab initio techniques have been used to explore the geometry of water molecules absorbed on the surfaces of the HAP crystal [32–34]. On the other hand, there has been very little computational effort devoted to the mechanical properties, presumably due to HAP's structural complexity and the accuracy required for computing ab initio mechanical properties at the atomistic level.

2.2. Elastic properties

HAP crystallizes in a hexagonal lattice (a, b and c axes) with the OH group oriented along the c-axis. For studying mechanical properties, it is more expedient to transform it into an orthorhombic cell (x, y and z axes) with the z-axis parallel to the c-axis as illustrated in Fig. 1. However, it is necessary to double the b-axis direction in order to maintain the periodicity of the lattice in the orthorhombic description. As a result, the simulation cell (hereafter

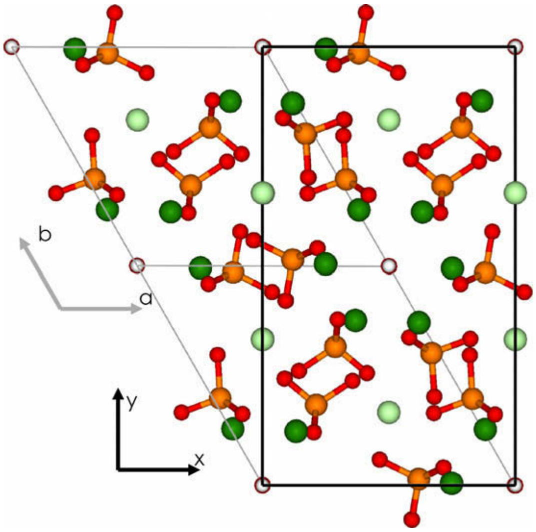

Fig. 1. Crystal structure of hexagonal and orthorhombic HAP. The light (heavy) green balls represent the columnar (axial) Ca ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)