Ab initio Simulation of Elastic and Mechanical Properties of Zn- and Mg-Doped Hydroxyapatite (HAP)

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Abstract

Hydroxyapatite (HAP) is an important bioceramic which constitutes the mineral components of bones and hard tissues in mammals. It is bioactive and used as bioceramic coatings for metallic implants and bone fillers. HAP readily absorbs a large amount of impurities. Knowledge on the elastic and mechanical properties of impurity-doped HAP is a subject of great importance to its potential for biomedical applications. Zn and Mg are the most common divalent cations HAP absorbs. Using density function theory based *ab initio* methods, we have carried out a large number of *ab initio* calculations to obtain the bulk elastic and mechanical properties of HAP with Zn or Mg doped in different concentration at the Ca1 and Ca2 sites using large 352-atom supercells. Detailed information on their dependence on the concentration of the substituted impurity is obtained. Our results show that Mg enhances overall elastic and bulk mechanical properties whereas Zn tends to degrade except at low concentrations. At a higher concentration, the mechanical properties of Zn and Mg doped HAP also depend significantly on impurity distribution between the Ca1 and Ca2 sites. There is a strong evidence that Zn prefers Ca2 site for substitution whereas Mg has no such preference. These results imply that proper control of dopant concentration and their site preference must be carefully considered in using doped HAP for specific biomedical applications.

Key words: Nanoscale hydroxyapatite, Zn-Mg doping, mechanical properties, site-preference, *ab initio* calculations

1. Introduction

Hydroxyapatite (HAP) is a bioceramic crystal constituting the major inorganic component of bone and teeth with superior biocompatibility with organic components such as collagen protein [1, 2]. It has been commonly used as fillers in place of amputated bone and also as coating in prosthetic implants [3]. HAP also has been used as an effective medium to store toxic waste [4]. However, pure synthetic HAP lacks mechanical strength for implants under load bearing conditions [5]. On the other hand, metallic implants which usually are much stronger and stiffer than the bone are more suitable under external stress but usually result in stress shielding effect, leading to osteoporosis phenomenon [6]. This may result in the loose contact with the bone over a period of time and ultimately leading to implant failure. In load bearing conditions, such as in dental implants, a functionally graded materials (FGM) could be a better alternative [7,8] since FGM can be tailored in such a way as to balance between biocompatibility of HAP and mechanical strength of the metal. It is therefore highly desirable to design FGM in contact with bone to be both biocompatible and sufficiently strong to bear the load.

HAP absorbs a large number of impurity ions and is seldom found in its stoichiometric pure form [9, 10]. The ion exchange ability of HAP promotes its biological activities and may result in significant change in its physical properties. The importance of impurity ions in HAP is reflected in numerous published works [9-12]. Most of the impurity ions that HAP absorbs and have biological significance are divalent metallic ions such as Zn^{2+} , Mg^{2+} , Pb^{2+} , etc. replacing Ca^{2+} ions in HAP which may also depend on the size of impurity ion [11,13]. The presence of impurities in HAP could affect its physical properties, either desirable or detrimental. Some of these cations in bone can actively participate in bone formation and reabsorption. For example, Mg^{2+} deficiency lowers the rate of growth of osteoblasts [14] leading to the decrease in bone mass density whereas Zn^{2+} promotes bone formation by increasing the rate of growth of osteoblasts [15]. Zinc doped HAP has also been found to exhibit protein adsorption [16].

Despite having superior biocompatibility, the major issue that limits HAP's current and further applications in biomedical arena is its weak mechanical properties as reflected in the lower values for the bulk mechanical moduli and elastic coefficients. Among the many published works on the effect of impurity presence in HAP to its physical properties [17-26], only a few of them partially address the changes in mechanical properties [20, 22]. For example, Zyman et al found that the micro hardness and compressive strength decreased in HAP with the addition of MgO [20]. On the other hand Tan et. al found that MgO can actually enhance mechanical properties in HAP depending on sintering temperature [22].

In order to fully understand the impurity effect on HAP, accurate theoretical modeling would be highly desirable as it has full control in determining impurity types and concentration at different atomic sites. The quantitative results obtained from theoretical computation based on quantum mechanics can be used for proper guidance to experimental work facilitating research in right direction without subject to costly trial and error approach. Furthermore, experimentally it is very difficult to control the exact doping locations of the impurity ions at specific sites at different concentration. There are many impurity ions HAP can accommodate [11] at different atomic sites and with different concentrations. Their effect on mechanical properties could be very different and some of them may be tailored for specific purposes such as for FGM

mentioned above. This is the area where modern large-scale simulation with sufficient predictive power can excel that could effectively aid the experimental work. Furthermore, accurate first-principles quantum mechanical calculation can provide a deeper fundamental understanding of the effects of the impurity doping at the atomic level which is so far missing.

In this work, we present the detailed *ab initio* calculations of the elastic and mechanical properties of divalent (Zn, Mg) doped HAP using large supercells up to a high concentration of 25% substitution of the total divalent Ca sites. In the next section, we briefly describe the methods used in the calculation. This is followed by the description of the results and discussion on the calculated elastic and mechanical properties of Zn/Mg doped HAP at different concentrations in the next section. In the last section, we end with a brief summary with some conclusions and pointing to the future tasks in this area.

2. Methods and Procedures of Computation

The Vienna *ab initio* simulation package (VASP) [27-29] is the primary computational tool used in this study. VASP is a density functional theory based method with plane wave basis set. It uses pseudopotential (PP) or projector augmented wave (PAW) methods with local density approximation (LDA) or generalized gradient approximation (GGA) for exchange correlation functional. In the present calculations, we used the PAW method [30, 31] with GGA PBE [32] for the exchange correlation functional which is considered to be more accurate. We used the 2 x 2 x 2 supercell of the hexagonal unit cell with 352 atoms for the doped HAP models with $a = b = 19.11915 \text{ \AA}$ and $c = 13.80124 \text{ \AA}$. All models are fully relaxed to high accuracy. Only the zone-center Γ point is used in the calculation since the cell is sufficiently large. A large energy cutoff of 600 eV is adopted and a conjugate-gradient algorithm is used for the ionic relaxation with a ionic convergence limit set to be $1.0\text{E-}5 \text{ eV/\AA}$.

We use a strain vs stress analysis approach [33, 34] for the elastic properties calculation. A small strain of $\pm 1\%$ is applied to each independent strain element in the fully relaxed structure. The magnitude of strain is carefully tested depending upon the nature of the material under consideration. Too small a strain enlarges computational noise and too large a strain may go beyond the elastic limit of the material which also results in inaccuracy. Our past experience for various crystals [34-39] and amorphous systems [40-44] indicate that $\pm 1\%$ of strain is the optimal choice for most structures under normal conditions. The fully relaxed structure under each applied strain is further relaxed by keeping its volume and cell shape fixed and the resulting stress tensor σ_{ij} are recorded. Once the required set of strain (ϵ_j) and the corresponding stress tensor (σ_{ij}) are obtained, the elastic stiffness constants C_{ij} are solved according to following equation.

$$\sigma_{ij} = \sum_{ij} C_{ij} \epsilon_j \quad (1)$$

From the elastic coefficients, parameters for the mechanical properties (bulk modulus K, shear modulus G, Young's modulus K and Poisson's ratio η) can be obtained from the so-called VRH polycrystalline approximation. The Voight approximation [45] assumed a uniform strain distribution throughout the structure and presented a way of calculating mechanical bulk properties and the Reuss approximation [46] assumed a uniform stress distribution. These two

assumptions gave the upper and lower limits of mechanical bulk properties and the average values of these two limits or the Hill approximation [47] are usually the results used to compare with measured data.

3. Results and Discussion

Hydroxyapatite has a complex hexagonal crystal structure (space group $P6_3/m$, No 176) with 44 atoms in its unit cell [48]. **Figure 1.** Shows the ball and stick diagram of the pure HAP unit cell structure and the $2 \times 2 \times 2$ supercell. There are two weakly bonded Ca sites denoted as Ca1 (columnar Ca, four sites) and Ca2 (axial Ca, six sites) which are the main host sites for divalent impurity ions. There are six tightly bonded PO_4 groups together with the partially occupied OH groups with occupation factor of 0.5 aligned along the crystallographic c-axis. The Ca1 site is surrounded by 6 PO_4 groups and Ca2 site is surrounded by 5 PO_4 groups and one OH group. The local environment of Ca1 is relatively symmetric in comparison to that of Ca2. Substitution of foreign ion at these two Ca sites affects the crystal structure differently therefore distribution of impurity ions between Ca1 and Ca2 sites could result in significant difference in their physical properties as well. The details of crystal structure of HAP have been discussed in many published works [11, 48-50].

3.1 Construction of Zn and Mg Doped HAP supercell models.

When impurity atoms are added to HAP replacing either Ca1 or Ca2 or both, the internal crystal symmetry is broken. There is no specific way to choose the sites for impurity substitution since there is no compelling evidence in the preference for substitution by Mg or Zn at one Ca site over the other. It is also not practical to cover all possible impurity configurations in large models as it is computationally prohibitive. Still, a reasonably large number of models are required to see a meaningful trend in the calculated physical properties.

In the present study, the impurities considered are only Zn or Mg with different concentrations ranging from 0 to 20 Zn/Mg atoms in the 352 atoms supercell with 80 Ca sites. We chose only even number of impurities and for each fixed number of impurity substitutions. There are different ways impurities Zn/Mg can be distributed them over the Ca1 and Ca2 sites. For example, for 6 impurity ions there are 7 ways (0-6, 1-5, 2-4, 3-3, 4-2, 5-1, and 6-0) to distribute them over Ca1 and Ca2 sites. The first (second) number in each set in the parenthesis represents number of Zn or Mg at the Ca1 (Ca2) sites. We further restrict the maximum number of impurities at each Ca site to be no more than 12. With this restriction, the number of possible impurity distributions over Ca1 and Ca2 sites progressively decreases for higher Zn/Mg concentration, since it is unlikely that impurity ions will concentrate only in one of the two Ca sites. For each set of impurity distribution, we constructed 30 models by randomly substituting Ca by Zn/Mg between Ca1 and Ca2 sites. All the 30 models were then fully relaxed using VASP. The model with the lowest total energy is taken as the representative model for that set and the model was further relaxed with higher accuracy for elastic properties calculations. **Table 1** shows the number of Zn/Mg atoms and the corresponding number of models for each concentration. The total number of supercell models screened and calculated is $2 \times 81 = 162$ in the present study. It must be made clear that the percentage of impurity substitution we mentioned to throughout this paper is referred to the available Ca sites in the supercell, not the

total number of the atoms in the supercell, or the weighted atomic percentage used in experimental samples.

With 81 impurity models each for Mg and Zn substitution over a reasonable number of site distributions, it is instructive to see if there is any site preference in the substitution. To this end, we analyze the total energy data for each model and list the results of the lowest energy and the difference from the pure HAP for the 6 set of Zn/Mg distributions in Ca1 or Ca2 sites. The results are listed in **Table 2**. For Mg substitution, there are 3 out of 6 cases where Ca1 is preferred (lower substitution energy) and 3 out of 6 cases where Ca2 is preferred. So for Mg substitution, there is no clear site preference. The case for Zn substitution is quite different, 5 out of the 6 cases prefer the Ca 2 site. This is the first time the information on the site preference for specific impurity substitution is revealed based on large scale *ab initio* modeling.

In **Figures 2 and 3**, we display the variation of lattice constants, cell volume and the mass density as a function of impurity concentration over the Ca sites for Zn- and Mg-doped samples. The error bar represents the standard deviation of the data set for each concentration. There is a considerable difference in the change in lattice constants (**Fig. 2**) between Zn- and Mg-doped HAP with concentration. In both cases, lattice constants decrease with increase in impurity concentration but the trend is smoother in the Mg-doped case. In the case of Zn substitution, a larger fluctuation in lattice constants is observed especially for *a* and *b* as a result of breaking the hexagonal symmetry. An interesting observation is that lattice *c* is nearly constant at lower Zn concentration but the decrease becomes more rapidly at higher Zn concentration. On the contrary, lattice *c* decrease smoothly with increasing concentration in the Mg-doped case. Unlike in Zn doped HAP, lattice *c* appears to be less unaffected by the distribution of Mg substitution between Ca1 and Ca2 sites. The difference in the lattice constant variations between Zn-doped and Mg-doped HAP can be partially explained by the site preference for Ca2 by Zn discussed earlier.

Figure 3 shows the change in volume (top) and mass density (bottom) with increasing Zn or Mg concentration. Despite the fluctuations in the change in lattice constants, volume decreases almost linearly for both Zn and Mg doped HAP. This is because Zn/Mg at Ca sites form shorter bonds with O atoms in PO₄ and OH groups. At higher Zn concentration, volume fluctuations start to become more significant depending upon the distribution between Ca1 and Ca2 sites. It should be noted that the change in density with increasing Zn is inversely proportional to change in volume since Zn is heavier than the Ca. **On the other hand, the near-constant density as a function of Mg substitution simply reflects the fact that the lighter Mg atom (compared with Ca) is compensated by concomitant reduction in the volume of the cell (shorter Mg-O bond length).**

In **Figure 4**, we plot the calculated total energy vs. impurities concentration for all Zn or Mg substituted models. The difference among the models is negligibly small and the total energy increased linearly with increasing Zn/Mg concentration. The rate of increase in energy with Zn substitution is much higher than that of Mg substitution indicating that HAP may absorb Mg in higher concentration than Zn. It should be pointed out that the purpose of this plot is for the comparison of the trends between Zn and Mg substitution as impurity concentration increased, not for the difference in the impurity formation energies in the two cases which require separate calculations and is clearly beyond the scope of this paper.

3.2 Calculated Elastic Constants for Zn- and Mg-doped HAP Supercells.

The calculated bulk elastic constants and mechanical properties of Zn- and Mg-doped HAP models averaged over different models for each concentration are presented in **Table 3** and **Table 4** respectively. The same data are also plotted in **Figure 5**. Since the substituted Zn or Mg makes shorter bonds with O atoms from PO_4 and OH groups, the alignment along the crystallographic c-axis is broken which diminishes the elastic stiffness along the c-axis. **Figure 6** shows the averaged C_{11} (top) and C_{33} (bottom) vs. the percentage concentration of Zn and Mg in a more fine scales along with standard deviation as error bar. In the Mg-doped case, C_{11} is enhanced with increased concentration while in the Zn-doped case, it decreases after the initial increase at 2.5%. On the other hand, C_{33} progressively decreases up to 15% of Zn concentration and then remains constant afterward. In the Mg-doped case, it slightly decreases up to 5 % of Mg concentration and then remains about the same afterward. This larger decrease in C_{33} with Zn-doped HAP in comparison to Mg-doped HAP as concentration increases results in considerable difference in the elastic anisotropy in these two cases. In other words, larger Zn concentration lowers linear elastic anisotropy whereas only a small decrease with Mg concentration. The error bars in **Figure 6** show the fluctuations in calculated data which depend on the relative distribution of Zn/Mg at the Ca1 and Ca2 sites for the given concentration. At higher Zn/Mg concentrations, there is higher fluctuation of both C_{11} and C_{33} . In pure HAP the average Ca-O bond length (BL) is 2.4161 Å (see Table 5 and 6). When Zn/Mg is doped in Ca sites, average Ca-O BL decreases slightly with increased Zn/Mg concentration. In both Zn and Mg doped HAP, the average BL of P-O bonds (in PO_4 groups) remains pretty much the same as expected. However, the average BLs of Zn-O and Mg-O bonds are significantly smaller than that of Ca-O bonds. The shorter BL of Zn-O/Mg-O results in Zn/Mg pulling O from PO_4 and OH groups. Since PO_4 tetrahedral and OH groups are tightly bonded, they move away slightly from their normal position (in comparison the pure HAP) towards Zn/Mg and structural alignment along the crystallographic c-axis gets distorted. This broken alignment along the crystallographic c-axis results in significant decrease in C_{33} .

Our calculation also shows that the average Zn-O BL range increases from 2.068 Å at 2 Zn substitution to 2.143 Å at 20 Zn substitution. The trend is opposite in case of Mg substitution. The average Mg-O BL range decreases from 2.212 Å at 2 Mg substitution to 2.190 Å at 20 Mg substitution. The reason they become shorter is because Ca is a larger ion compared with Zn and Mg and their interaction with O and other atoms in the substituted crystal are different as reflected in the ab initio quantum mechanical calculation.

The shear elastic anisotropy, or the difference between C_{44} and C_{66} , reveals a different story (see **Figure 7**). Zn doped case has a lower anisotropy as impurity concentration increases compared with Mg-doped case. Therefore Zn substitution degrades the overall elastic stiffness but also lowers the shear elastic anisotropy which could be important in some application as composites. On the other hand Mg substitution enhances the overall elastic constants with only a slightly lowered elastic anisotropy, making it more useful when anisotropy and larger C_{33} are key materials parameters. For Mg, both C_{44} and C_{66} increase gradually with concentration but with larger fluctuations in C_{44} than in C_{66} , depending on Mg distribution between the two Ca sites. In

the case of Zn substitution, C_{44} increases slightly up to 2.5 % of Zn and decrease afterwards with large fluctuation.

We are not aware of any published data on the elastic constants of Zn- or Mg-doped HAP either measured experimentally or calculated theoretically.

3.3 Polycrystalline Bulk Mechanical Properties.

Polycrystalline bulk mechanical properties are calculated from the elastic stiffness constants and compliance tensor. **Figure 8** shows the variation of calculated bulk modulus (K), (top panel), shear modulus (G) (middle panel), and Young's modulus (E) (bottom panel) vary with Zn or Mg concentration. In general, at low concentration (< 2.5 %), K, G, E are all enhanced in both cases. However, the similarity ends here. Above 2.5 %, moduli K, G, E all decreases significantly with increasing Zn concentration. The trend is opposite, with Mg concentration. They actually increase slowly for concentration above 2.5%. The large error bar at high concentration indicates the moduli values dependent on the distribution of Zn or Mg among Ca1 and Ca2 sites. The resulting fluctuation is more for Zn doped case than in Mg doped case.

To gain additional insights on the variation in bulk moduli (K, G and E) with Zn and Mg distribution between Ca1 and Ca2 sites, we illustrate it in contour plots shown in **Figure 9**. Over all, bulk modulus is smaller for higher Zn concentration at Ca2 sites but K is slightly larger for higher Mg concentration at Ca2 sites. The contour plots for shear and Young's modulus shown in the middle and bottom panels respectively are somewhat similar to that of bulk modulus K. Higher Zn concentration in Ca2 sites has slightly smaller G and E but the trend is less clear for Mg-doping. On average, higher Mg concentration tends to have slightly larger G and E for substitutions at the Ca2 site.

There is a scarcity of data on the measured mechanical properties of Mg or Zn doped HAP with well characterized samples [22, 51]. They usually describe the way how they were prepared with rudimentary information on compositions and no direct description on structures and as such they are not easy to compare with on simulated data on with emphasis on the atomic scale structures and accurate ab initio calculations. Tan et al [22] presented measured Young's modulus of MgO-doped HAP with different weight % at different sintering temperatures. There is a large variation in E with sintering temperature and its effect on the internal structural adjustment that takes place as sintering temperature varies is not clear. Over all they found MgO in HAP enhanced E with unusually largest value of 136.6 GPa for 1 wt% at sintering temperature of 1150°C. Comparing with our simulation data on Mg-doped HAP, there is a reasonable agreement in the overall trend with this measured data. The calculated E (108GPa to 110GPa) based on VRH approximation is somewhat smaller than the larger measured E value (136.3 GPa). Some of the measured E values at different temperature are closer to our calculated data.

The calculated Poisson's ratio (η) presents a more comprehensive but more complicated assessment of the average bulk mechanical properties since it depends on both the bulk and shear moduli. A conventional and simple interpretation of Poisson's ratio is that it is a measure of the resistance to change in bond length in relation to the resistance to change the bond angle. In general, larger Poisson's ratio results from the larger K and smaller G which means the

structure is relatively ductile as crystal planes can slip more easily. On the other hand smaller η could be interpreted as the material to be relatively more brittle material. In **Figure 10 (top)**, we plot the Poisson's ratio η as a function of Zn and Mg concentration. At lower concentration, η does not fluctuate much and the averaged value is close to that of pure HAP. At higher concentration, η increases significantly with Zn concentration but only slightly with Mg concentration. In case of Zn substitution, the large fluctuation in η at higher concentration is related to the higher fluctuation in K discussed above. In **Figure 10 (bottom)**, we display the contour plot for η similar to those of **Figure 9** for the individual moduli. This plot provides the information on how η changes with Zn and Mg distribution between Ca1 and Ca2 sites. At higher Zn concentration, η is significantly larger at the Ca1 sites than at the Ca2 sites. This result is quite important since it indicates that the distribution of Zn between the Ca1 and Ca2 sites plays a role in determine the relative brittleness of doped HAP crystal. For Mg distribution, there is no clear cut evidence but more Mg at the Ca1 site has slightly larger η indicating the possibility of a relatively more brittle structure.

4. Summary and Conclusions

We have calculated the elastic and mechanical properties of Zn- and Mg-doped HAP for impurity doping up to 25% of total Ca sites. The result and trend presented is the first time in providing atomic-scale understanding of how the elastic properties evolve in HAP with increased Zn/Mg doping. Based on a large number of accurate *ab initio* calculations and careful statistical analysis of the data, it is concluded that Zn substitution prefers the Ca2 site in HAP whereas Mg substitution has no such preference. This is a significant step beyond the current studies on stoichiometric HAP crystal [50, 53, 54], its vacancies or low doping concentrations. Our simulation shows that Zn/Mg doping in HAP results in the formation of shorter Zn-O and Mg-O bonds. For Zn substitution, both lattice parameters a and c depend significantly on the Zn distribution between Ca1 and Ca2 sites whereas for Mg-doping, there is a smaller dependency for a and no dependency for c . This change in lattice parameters is also reflected in the calculated elastic constants. Over all, Mg-doping enhances elastic properties of HAP whereas Zn-doping degrades it. This degradation is the consequence of the broken alignment of PO₄, OH and Ca sites along the crystallographic c -axis due to the decreased bond lengths of Zn/Mg with O atoms. Also, Zn-doping lowers elastic anisotropy far more than Mg-doping. Assuming isotropy is pivotal for the reduction of elastic stiffness especially the C_{33} , then Zn-doped HAP may have some promising applications. On the other hand, if anisotropy is not an issue, then Mg-doped HAP looks more desirable based on their overall mechanical properties. Such information can explain many of the experimental observations for metal doped HAP crystal as bioceramics implants.

It is fitting to comment on possible further simulations on HAP and other bioceramics. Clearly, large-scale simulation can play a critical role in understanding the mechanical properties of doped biomaterial systems and provide crucial information to the synthesis and characterization of these complex materials important in biomedical applications. We intend to use similar approach to investigate other challenging issues such as porosity, nature of electronic structure and bonding, interactions of HAP and other inorganic crystals with organic counterparts such as collagen and other proteins. For such studies, another highly effective *ab initio* method [55, 56]

using atomic orbitals in the basis expansion will be used in conjunction with the plane-wave based VASP code.

Acknowledgments

This research was supported initially by DOE under DE-FG-0284DR45170 in the early phase of the work and more recently and partially by DOE-Office of BES, Division of Materials Science and Engineering under the grant DE-SC008176. This research used the resources of NERSC supported by the Office of Science of DOE under contract No. DE-AC03-76SF00098.

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Table 1. Zn and Mg Concentration and Corresponding Number of HAP Models.

No. of Zn	Number of Models	No. of Mg	Number of Models
0	1	0	1
2	3	2	3
4	5	4	5
6	7	6	7
8	9	8	9
10	11	10	11
12	13	12	13
14	11	14	11
16	9	16	9
18	7	18	7
20	5	20	5
Total	81	Total	81

Table 2. Site preference of substitution at Ca1 or Ca2 site from the total energies based on distribution. Shaded row indicates lower substitution energy (preferred cite)

No. of impurities	at Ca1 Sites	at Ca2 Sites	Zn		Mg	
			Total E (eV)	E-E0	Total E (eV)	E-E0
0	0	0	-2495.6755	0.0000	-2495.6755	0.0000
2	0	2	-2484.8641	10.8114	-2485.7138	9.9617
2	2	0	-2484.8347	10.8408	-2485.6923	9.9832
4	0	4	-2473.9163	21.7592	-2481.5916	14.0839
4	4	0	-2473.9655	21.7100	-2481.6144	14.0611
6	0	6	-2463.2812	32.3943	-2477.5736	18.1019
6	6	0	-2463.1871	32.4884	-2477.4911	18.1844
8	0	8	-2452.3471	43.3284	-2473.5410	22.1345
8	8	0	-2452.2499	43.4256	-2473.3423	22.3332
10	0	10	-2441.5901	54.0854	-2469.0406	26.6349
10	10	0	-2441.0592	54.6163	-2469.1319	26.5436
12	0	12	-2430.4937	65.1818	-2465.1123	30.5632
12	12	0	-2430.1303	65.5452	-2465.2075	30.4680

Note, shaded bar indicates averaged lower energy for substitution at Ca 1 (second column) and Ca2 (third column). For Mg substitution, no particular preference between Ca1 and Ca2. For Zn substitution, Ca2 is the preferred site.

Table 3. Calculated elastic constants and mechanical bulk properties (in GPa) of Zn doped HAP models. The data shown is the averaged data for each concentration.

% of Zn	C ₁₁	C ₃₃	C ₄₄	C ₆₆	C ₁₂	C ₁₃	K	G	E	η
0.00	122.159	166.602	42.074	44.411	34.423	65.177	79.488	41.734	106.554	0.277
2.50	125.443	158.436	42.516	44.180	36.818	62.867	79.874	42.019	107.249	0.276
5.00	125.074	154.414	41.569	43.892	37.992	61.524	79.314	41.397	105.786	0.278
7.50	125.248	147.673	41.892	43.557	39.008	59.368	78.323	41.293	105.360	0.276
10.00	124.779	141.989	41.588	42.675	39.148	58.358	77.406	40.680	103.847	0.276
12.50	124.588	137.466	40.801	42.145	39.639	57.792	76.871	39.951	102.146	0.279
15.00	124.417	134.864	40.355	41.477	39.990	57.577	76.570	39.440	100.976	0.280
17.50	124.120	134.536	40.014	41.126	40.735	58.222	76.898	39.014	100.104	0.283
20.00	122.836	132.775	39.610	40.259	41.224	56.117	75.676	38.711	99.204	0.281
22.50	123.718	134.260	39.424	40.690	41.961	58.325	77.116	38.516	99.049	0.286
25.00	122.837	135.010	39.877	39.988	40.949	58.517	76.763	38.536	99.024	0.285

Table 4. Calculated elastic constants and mechanical bulk properties (in GPa) of Mg doped HAP models. The data shown is the averaged data for each concentration.

% of Mg	C ₁₁	C ₃₃	C ₄₄	C ₆₆	C ₁₂	C ₁₃	K	G	E	η
0.00	122.159	166.602	42.074	44.411	34.423	65.177	79.488	41.734	106.554	0.277
2.50	125.504	164.367	42.163	44.510	35.921	64.958	80.750	42.066	107.525	0.278
5.00	126.506	161.992	42.765	44.664	36.704	64.633	81.011	42.329	108.150	0.277
7.50	127.243	160.871	43.433	44.909	37.084	64.407	81.186	42.678	108.943	0.276
10.00	127.876	160.614	42.907	44.820	37.968	64.119	81.499	42.524	108.670	0.278
12.50	128.729	160.237	43.302	44.593	38.353	64.693	82.026	42.613	108.968	0.279
15.00	128.619	160.769	43.012	44.772	38.570	64.693	82.090	42.540	108.821	0.279
17.50	129.283	160.451	42.957	45.002	39.383	64.813	82.540	42.573	108.981	0.280
20.00	129.318	162.107	43.111	44.626	39.343	64.919	82.694	42.667	109.216	0.280
22.50	130.026	161.518	43.784	45.201	40.567	64.800	83.149	43.060	110.161	0.279
25.00	131.118	160.777	43.528	45.226	41.417	64.328	83.461	43.066	110.235	0.280

Table 5. Average bond length ($\text{\AA}$) of Ca-O bonds, P-O bonds, O-H bonds and Zn-O bonds in Zn doped HAP. Only nearest neighbor bonds are considered.

Zn	Ca-O avBL	P-O avBL	O-H avBL	Zn-O avBL
0	2.4161	1.5547	1.7251	0.0000
2	2.4153	1.5551	1.6673	2.0676
4	2.4133	1.5551	1.5816	2.0907
6	2.4113	1.5550	1.4854	2.0905
8	2.4090	1.5551	1.4953	2.1005
10	2.4078	1.5552	1.4760	2.1190
12	2.4068	1.5552	1.4881	2.1268
14	2.4045	1.5553	1.4792	2.1370
16	2.4025	1.5555	1.4893	2.1336
18	2.4003	1.5557	1.4423	2.1502
20	2.3999	1.5558	1.4812	2.1425

Table 6. Average bond length ($\text{\AA}$) of Ca-O bonds, P-O bonds, O-H bonds and Mg-O bonds in Zn doped HAP. Only the nearest neighbor bonds are considered.

Mg	Ca-O avBL	P-O avBL	O-H avBL	Mg-O avBL
0	2.4161	1.5547	1.7251	0.0000
2	2.4145	1.5550	1.6056	2.2122
4	2.4128	1.5550	1.5279	2.2075
6	2.4106	1.5548	1.5147	2.2055
8	2.4075	1.5548	1.4724	2.2021
10	2.4062	1.5549	1.5370	2.2037
12	2.4039	1.5547	1.5305	2.1992
14	2.4021	1.5548	1.5352	2.1973
16	2.3996	1.5548	1.5560	2.1947
18	2.3990	1.5546	1.5630	2.1888
20	2.3956	1.5546	1.4921	2.1898

Figure 1. Top: Ball and stick diagram of unit cell of HAP in hexagonal symmetry. Bottom: 352-atoms supercell of HAP.

Figure 2. Averaged lattice constants of Zn- (a) and Mg- (b) doped HAP at different concentrations.

Figure 3. Calculated volume (top) and mass density (bottom) of Zn- and Mg-doped HAP.

Figure 4. Calculated total energy of Zn- and Mg-doped HAP at different concentrations.

Figure 5. Calculated average C_{ij} of Zn-doped HAP (top) and Mg-doped HAP (bottom) at different concentrations.

Figure 6. Calculated C_{11} (top) and C_{33} (bottom) of Zn- and Mg-doped HAP at different concentrations.

Figure 7. Calculated C_{44} (top) and C_{66} (bottom) of Zn- and Mg-doped HAP at different concentrations.

Figure 8. Calculated bulk modulus (top), shear modulus (middle) and Young's modulus (bottom) of Zn- and Mg-doped supercell HAP models. Error bars denote the standard deviation.

Figure 9. Contour plot of variation in bulk Modulus (top panel), shear Modulus (middle panel), and Young's Modulus (bottom panel) for Zn-doped (left side) and Mg-doped right side) as a function of impurity concentrations between Ca1 and Ca2 sites.

Figure 10. Top: Calculated Poisson's ratio (η) of Zn and Mg doped HAP at different concentrations. Bottom: Contour plot of variation in Poisson's ratio with Zn-doping (left) and Mg-doping as a function of impurity concentrations between Ca1 and Ca2 sites.