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Crystal Structure of Ba-Doped α-Tricalcium Phosphate $(Ca_{1-x}Ba_x)_3(PO_4)_2$

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Introduction

Tricalcium phosphate [TCP: $Ca_3(PO_4)_2$] is one of the most important biomaterials for bone substitute applications as well as apatites. Far less attention has been devoted to the crystal structure of non-doped and doped α-TCP, probably due to its complicated structure. The purpose of the present study is to investigate the unit cell parameters and site occupancy of Ba-substituted α-TCP, $(Ca_{1-x}Ba_x)_3(PO_4)_2$ (x = 0.05, 0.10 and 0.15), through a high-angular-resolution synchrotron powder diffractometer. This work was published in M. Yashima and Y. Kawaike, *Chem. Mater.* **19**, [17] 3973-3979 (2007).

Experiments

Single phase of alpha barium-substituted tricalcium phosphate (Ba-α-TCP) $(Ca_{1-x}Ba_x)_3(PO_4)_2$ (x=0.05, 0.10 and 0.15) has been prepared by solid-state reactions. Synchrotron x-ray powder diffraction experiments of α-TCP, $(Ca_{1-x}Ba_x)_3(PO_4)_2$ (x = 0.05, 0.10 and 0.15) were performed at 298 K using the multiple-detector system installed at the BL-4B$_2$ beam line of the Photon Factory, KEK, Japan. A monochromatized 1.20628(4) Å x-ray beam was utilized. The crystal structure of the $(Ca_{1-x}Ba_x)_3(PO_4)_2$ was refined by the Rietveld method with a computer program RIETAN-2000 (Izumi & Ikeda, 2000).

Results and discussion

Diffraction data were successfully analyzed by the single phase Ba-α-TCP (space group $P2_1/a$). The calculated intensity agreed well with the observed data. For example, for the $(Ca_{0.85}Ba_{0.15})_3(PO_4)_2$ composition, the reliability factors were R_{wp} = 5.42%, R_p = 4.13%, S = 1.94, R_I = 2.73% and R_F = 1.92%. Unit-cell parameters a, b, c and β increase with increasing Ba content. The unit cell volume also increases with Ba content (Fig. 1), which is ascribed to the substitution of Ca atoms by the larger-sized Ba atoms. Figure 2 shows the crystal structure of Ba-substituted α-TCP, $(Ca_{0.85}Ba_{0.15})_3(PO_4)_2$, depicted with the refined crystallographic parameters. The Ba atoms are substituted for the Ca sites. Most of the Ba atoms are located at three crystallographic sites, namely, Ca17: (0.0909(6), 0.4167(2), 0.7823(5)) g(Ba)=0.72(2); Ca11: (0.4068(6), 0.2506(2), 0.2199(5)) g(Ba)=0.67(1); Ca5: (0.0983(6), 0.0837(2), 0.7857(5)) g(Ba)=0.65(1) among the eighteen cation sites in the α-$(Ca_{0.85}Ba_{0.15})_3(PO_4)_2$. Here, g(Ba) is the occupancy factor of Ba atoms. These sites have relatively smaller bond valence sums, indicating the preference sites for the larger-sized Ba substitutions.

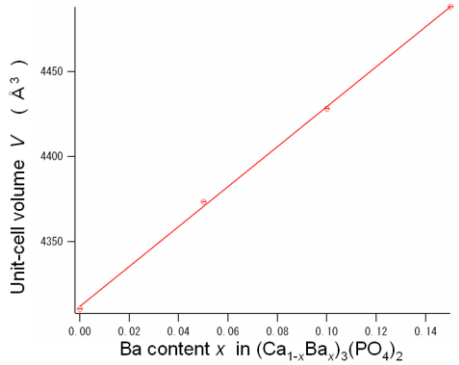

Fig.1. Compositional dependence of unit-cell volume of α-TCP, $(Ca_{1-x}Ba_x)_3(PO_4)_2$.

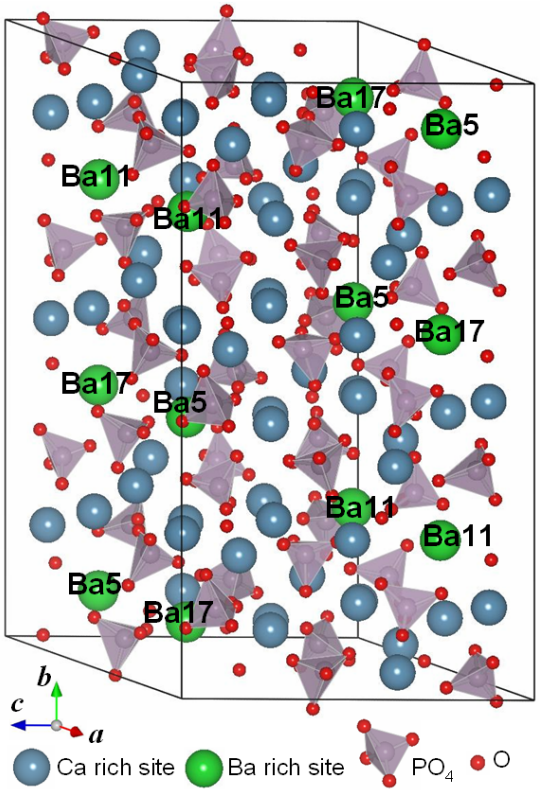

Fig.2. Refined crystal structure of Ba-substituted α-TCP, $(Ca_{1-x}Ba_x)_3(PO_4)_2$ (x=0.15)

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