^{43}Ca NMR of Substituted Tricalcium Phosphate for Waste Immobilisation

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Introduction

β-tricalcium phosphate, $Ca_3(PO_4)_2$, (β-TCP),is being investigated as a host material for intermediate level radioactive waste. There are five calcium sites in the crystal structure: 3 in (18b) sites, Ca(1), Ca(2) and Ca(3) coordinated to 7, 8 and 8 oxygens respectively with Ca-O mean bond lengths ranging from 2.43 – 2.54 Å; 1 in a (6a) site, Ca(5) with 6 oxygens at a mean Ca-O distance of 2.26 Å; and 1 in an ~ half occupied (6a) site, Ca(4) with 3 oxygens at 2.53 Å. It is thought that waste cations will substitute for Ca on different sites depending largely on the ionic radius of the cation – i.e. small cations occupying the Ca(5) site and large cations the Ca(1), Ca(2) and Ca(3) sites. The occupancy of the Ca(4) site changes in a way which depends on the mechanism of doping, the charge on the cations and whether co-doping is performed. Characterisation of doped systems has relied on X-ray diffraction techniques to date. We have used ^{31}P MAS NMR, which is remarkably sensitive to changes on the calcium sites. However, the interpretation of the ^{31}P NMR in terms of the changes to the calcium sites is challenging and it would be of great benefit to observe the calcium environment directly.

Experimental

Samples are of the general formula $Ca_9M_x(PO_4)_{6+x}$ with M being a trivalent cation. Substitution of M^{3+} for Ca^{2+} is thought to lead to the creation of more vacancies on Ca(4). MAS NMR was performed using the 31mm bore, 19.6T magnet (830MHz ^{1}H) operated with a Bruker DRX console. An NHMFL-built, 7mm probe was used with MAS frequency 5kHz. An adiabatic pulse enhancement scheme was employed (5ms, 5kHz CHIRP sweep 250kHz below the CT frequency where the probe is tuned, ~20kHz rf). Spectra were acquired using a 3μs excitation pulse, a 4s pulse delay and referenced to 1M $CaCl_2$ solution.

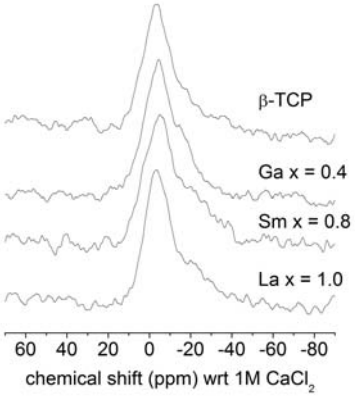

Figure 1. ^{43}Ca NMR spectra from variously doped β-TCP samples.

Results and Discussion

Figure 1 shows the spectra obtained from samples with different levels of doping with Ga^{3+} (Ga(IV)-O = 1.84 Å), Sm^{3+} (Sm(VIII)-O = 2.45 Å), La^{3+} (La(VII)-O = 2.49 Å). Figure 2 shows the fit to the spectra from pure β-TCP and $Ca_9Ga_{0.8}(PO_4)_{6.8}$ where the areas of the peaks have been constrained according to the following models:

Pure β-TCP – According to the crystal structure Ca(1):Ca(2):Ca(3):Ca(4):Ca(5) peak area ratios should be 18:18:18:~3:6. Three Gaussians of equal area were fit to the large central feature and two further peaks to the wings. The observed ratios are 17.5:17.5:17.5:4.2:6.4 (error ± 1).

$Ca_9Ga_{0.8}(PO_4)_{6.8}$ – If Ga substitutes on Ca(5), as expected from its size, the Ca(1):Ca(2):Ca(3):Ca(4):Ca(5) peak area ratios should be 18:18:18:0.6:1.2. Three Gaussians of equal area were fit to the large central feature and one further peak in the downfield wing. This gave the ratios 18:18:18:0:1.8.

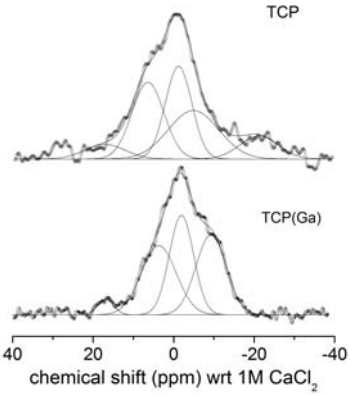

Figure 2. Initial fits to spectra of pure β-TCP and Ga doped β-TCP.

Conclusions

Natural abundance ^{43}Ca spectra can be simulated with suitable models of the calcium distribution in substituted β-TCP. Further work using ^{43}Ca isotopically enriched samples should be pursued to obtain spectra with improved S/N and provide fits with greater confidence.

Acknowledgements

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