# X-Ray, Ir and Magnetochemical Studies on Calcium Manganese Hydroxyapatites

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Manganese hydroxyapatite, MnHA and its solid solutions with calcium hydroxyapatite CaHA, have been synthesised. The effect of substitution of manganese in CaHA is studied by X-ray, ir and magnetochemical studies. The formation of homogeneous solid solutions of CaHA and MnHA is indicated from the measurement of lattice constants. In the ir spectra, the internal modes of the $PO_4$ ion are shifted to lower frequencies consequent upon increase in cation mass and cation-anion bond strength. MnHA and its solid solutions with CaHA are found to be paramagnetic.

THE ability of calcium hydroxyapatite, $Ca_{10}(PO_4)_6$-$(OH)_2$, (CaHA) as a host material allowing various cationic exchange reactions[1] in it is well-documented. Manganese can be incorporated into CaHA, consequent upon the closeness of its ionic radius (0.80 Å) with that of calcium (0.99 Å), through $Ca^{2+} \rightarrow Mn^{2+}$ exchange reaction. This exchange when forced to completion, results in the formation of manganese hydroxyapatite, $Mn_{10}(PO_4)_6(OH)_2$, (MnHA), while incomplete substitution leads to calcium manganese hydroxyapatites, $Ca_{10-x}Mn_x$-$(PO_4)_6(OH)_2$, where x is the compositional parameter ranging from 1 to 10. Several recent papers[2] dealing with manganese chlor- and fluor-apatites have appeared in literature. Ohkubo[3] in his studies on manganese halophosphates indicated the presence of $Mn^{2+}$ ions over the two non-equivalent $Ca^I$ and $Ca^{II}$ apatite crystallographic sites. Since no information is available on solid solutions of CaHA and MnHA, we are interested in synthesising them in aqueous media and their characterisation by X-ray, ir and magnetic susceptibility measurements. Such compounds are considered important since calcium hydroxyapatite doped with manganese are useful luminescence and laser materials[4].

## Experimental

The solid solutions of calcium and manganese hydroxyapatites were prepared by precipitation at 100° at pH 7.4,

$$(10-x)Ca^{2+} + xMn^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow$$
$$Ca_{10-x}Mn_x(PO_4)_6(OH)_2 \quad (1)$$
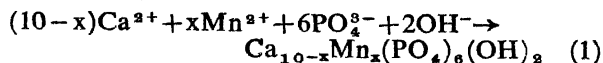
Stock solutions of $MnAc_2$, $CaAc_2$ and $NH_4H_2PO_4$ were prepared in $CO_2$-free conductivity water and their Mn, Ca and P contents determined. As per the stoichiometry in equation (1), appropriate volumes of the mixed cation solution was added dropwise to the phosphate solution maintained at pH 7.4 and 100°. A 0.05 M NaOH solution was added dropwise to maintain the pH constant during precipitation. $CO_2$-free $N_2$ gas was bubbled through the reaction medium to eliminate the possibility of formation of carbonate apatite. The precipitates were refluxed for 4 h in contact with the mother liquor, centrifuged and washed till the washings were free from Ca, Mn and P ions. The precipitates were then stirred with a 2% solution of EDTA at pH 7.4 for 2 h, filtered, washed well and dried at 800° for 6 h.

Phosphorus in the samples was determined spectrophotometrically[5] as phosphomolybdate. The combined Ca and Mn in the filtrate was determined complexometrically in presence of 5% $NH_2OH$. In another experiment containing Ca and Mn, the former was masked by $NH_4F$ and manganese alone was determined complexometrically and the calcium content known by difference. The average error (wt%) was found to be Ca : ±0.5, Mn : ±1.00, P : ±1.00.

The X-ray diffractograms were obtained on a Phillips unit with X-rays generated with 45 kV and 25 MA on a Cu target using Ni filter. The scattering region 20−40° 2θ was surveyed since this included the main diffraction profile. The ir spectra (KBr) were recorded on a Perkin-Elmer double grating spectrophotometer. The magnetic susceptibility measurement was carried out by using Gouy's method at 30°.

## Results and Discussion

The molecular formulas of the samples calculated from the analytical data are given in Table 1. The molar g-atom ratio, (Ca+Mn)/P, are found in the range 1.63−1.67 (theo. for apatites, 1.667).

The X-ray diffractograms of the samples possessed a line distribution typical of apatites. The diffractograms decreased in their sharpness and intensity with increase in manganese content of the

TABLE 1—ANALYTICAL DATA OF CALCIUM HYDROXYAPATITE, MANGANESE HYDROXY APATITE AND THEIR SOLID SOLUTIONS

| Sl. no. | Molecular formula | Analysis % : Found/(Calcd.) | | | g-atom ratio (Ca+Mn)/P |
|---|---|---|---|---|---|
| | | Ca | Mn | P | |
| 1. | $Ca_{10}(PO_4)_6(OH)_2$ | 39.82 (39.84) | — | 18.41 (18.52) | 1.67 |
| 2. | $Ca_9Mn_1(PO_4)_6(OH)_2$ | 35.33 (35.33) | 5.39 (5.39) | 18.29 (18.25) | 1.65 |
| 3. | $Ca_8Mn_2(PO_4)_6(OH)_2$ | 30.06 (30.95) | 10.63 (10.62) | 17.60 (17.99) | 1.63 |
| 4. | $Ca_7Mn_3(PO_4)_6(OH)_2$ | 26.69 (26.69) | 15.63 (15.72) | 17.73 (17.73) | 1.65 |
| 5. | $Ca_6Mn_4(PO_4)_6(OH)_2$ | 22.59 (22.56) | 20.64 (20.66) | 17.44 (17.49) | 1.66 |
| 6. | $Ca_5Mn_5(PO_4)_6(OH)_2$ | 18.57 (18.54) | 25.44 (25.46) | 17.23 (17.24) | 1.67 |
| 7. | $Ca_4Mn_6(PO_4)_6(OH)_2$ | 14.65 (14.63) | 30.13 (30.14) | 17.00 (17.01) | 1.66 |
| 8. | $Ca_3Mn_7(PO_4)_6(OH)_2$ | 10.84 (10.82) | 34.68 (34.69) | 16.77 (16.78) | 1.66 |
| 9. | $Ca_2Mn_8(PO_4)_6(OH)_2$ | 7.13 (7.12) | 39.11 (39.13) | 16.52 (16.56) | 1.66 |
| 10. | $Ca_1Mn_9(PO_4)_6(OH)_2$ | 3.52 (3.51) | 43.42 (43.43) | 16.33 (16.34) | 1.67 |
| 11. | $Mn_{10}(PO_4)_6(OH)_2$ | — | 47.63 (47.62) | 16.12 (16.13) | 1.65 |

TABLE 2—LATTICE CONSTANTS, CELL VOLUME, $D_c/D_a$, DENSITY AND AVAGODRO NUMBER OF THE SAMPLES

| Sl. no.* | Lattice constants (Å) | | Cell volume (Å³) | $D_c/D_a$ | Density g cm⁻³ | $N_A$ ×10⁻²³ |
|---|---|---|---|---|---|---|
| | a | c | | | | |
| 1. | 9.44 | 6.88 | 530.96 | 1.27 | 3.14 | 6.02 |
| 3. | 9.42 | 6.85 | 527.49 | 1.17 | 3.25 | 6.03 |
| 5. | 9.41 | 6.82 | 523.54 | 1.01 | 3.37 | 6.02 |
| 7. | 9.40 | 6.80 | 520.82 | 1.10 | 3.48 | 6.02 |
| 9. | 9.38 | 6.78 | 517.63 | 1.10 | 3.60 | 6.02 |
| 11. | 9.37 | 6.76 | 514.54 | 0.90 | 3.72 | 6.02 |

*As in Table 1.

samples. The line broadening measurements on the 300 and 002 reflections showed that both the a and c axes dimensions decreased with increase in manganese in the solid solutions. Consequent upon the substitution of Mn in CaHA, the cell volume of the samples decreased (Table 2) due to the contraction in the lattice parameters.

The analyses of the samples exhibited a decrease in calcium with increase in manganese content. Since, the inclusion of manganese in the samples is accompanied by a systematic lattice parameter change and exclusion of calcium, it can be said that manganese is substituted for calcium in CaHA. Further, though an impurity ion either as a substituent in CaHA or not, can affect the crystallite size and morphology, but only as a substituent can it affect the a and c parameters of CaHA. Therefore, Mn ions are present in the samples as a substituent. The dimensions along the a and c axes respectively are determined using the Scherrer formula : $D = 57.3$ $K' \lambda/\beta_{1/2} \cos \theta$, where, $K' = 0.2$, $\lambda = 1.54$, $\beta_{1/2}$ is the width at one half maximum height of the peak and $\theta$ is one of the scattering angle. The length to width ratio, $D_o/D_a$ remained almost constant. This therefore indicates that the lattice of CaHA changed

its dimension with change in composition in the same proportion as the changes in the a and c direction and further, that the cations in the samples are statistically distributed[6] at each of the cation sites of the apatite structure. With the regular decrease in lattice parameters, the points on Fig. 1 fall on a straight line. This system, therefore followed Vegard's law, indicating the formation of continuous solid solutions.

The infrared spectra of the samples exhibited in general absorptions corresponding to $\nu_1$ (962 cm⁻¹), the non-degenerate P−O symmetric stretching mode ; $\nu_2$ (468 cm⁻¹), the O−P−O bending mode ; $\nu_{3a}$ (1 090 cm⁻¹), $\nu_b$ (1 035 cm⁻¹), the antisymmetric P−O stretching mode ; $\nu_{4a}$ (600 cm⁻¹), $\nu_{4b}$ (555 cm⁻¹), the O−P−O bending mode ; and the hydroxyl stretching $\nu_s$ mode at 3 570 cm⁻¹. The effect of substitution of Ca by Mn in CaHA resulted in a shift of the internal phosphate and $\nu_s$ hydroxyl modes to lower frequencies. In case of MnHA, the $\nu_1$, $\nu_2$, $\nu_{3a}$, $\nu_{3b}$, $\nu_{4b}$, $\nu_{4a}$ PO₄ vibrations and $\nu_s$ (OH) mode are recorded at 955, 450, 1 070, 1 020, 560, 585 and 3 550 cm⁻¹ respectively. The splitting of the $\nu_3$ (PO₄) vibration is however found to be pronounced. This is due to the more covalent
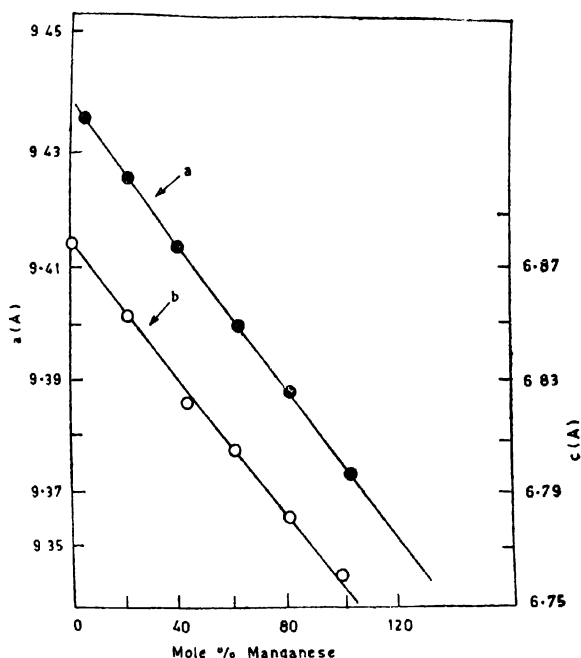
Fig. 1. Dependence of lattice constants $a$ and $c$ on the composition of samples.

cation-anion bond character in MnHA compared to CaHA, consequent upon the greater polarising power of Mn (3.21) than Ca (2.04). As the cation-anion bond becomes stronger, the frequencies of the internal modes of the anion should become cation-dependent and in turn more sensitive to cation mass. This predominantly contributed to

lowering frequencies. Similar observations were made by Bhatnagar[7] and Klee and Engel[8].

CaHA is found to be diamagnetic while MnHA and its solid solutions with CaHA are paramagnetic. A gradual increase in the molar paramagnetic susceptibility is observed with increase in manganese in the samples. The $\mu_{eff}$ values for all tne samples are found in the range $5.94 - 6\,01$ B.M., indicating the divalent state of manganese in the solid solutions synthesised.

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